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Reviewing the literature from July 1996 to December 1997

Previous review: C. P. Dell, *Contemp. Org. Synth.*, 1997, 4, 87

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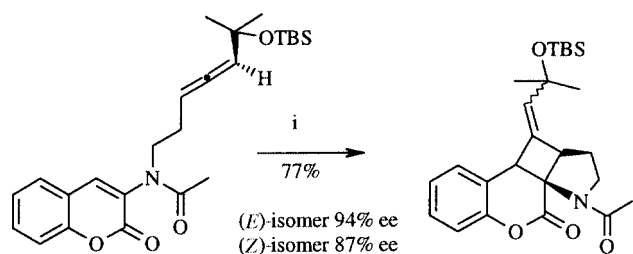
1 Introduction

A number of review articles, either specifically on cycloadditions, or incorporating cycloadditions as a major theme in their articles have appeared recently. The preparation of 1-oxabicyclo- β -lactam antibiotics *via* [2 + 2] cycloadditions of isocyanates to sugar vinyl ethers has been published.¹ Dimethyleneketene acetals react with olefins and [60]fullerene in a [2 + 2] sense and the utility of such ketene acetals as cyclopropane-carboxylate synthons has been reviewed.² In the [3 + 2] cycloaddition field, articles on metal-catalysed asymmetric cycloadditions,³ 1,3-dipolar additions to allenes,⁴ stereoselection in the dipolar addition to alkenes bearing an allylic stereocentre,⁵ asymmetric cycloadditions of nitrones with alkenes⁶ and dipolar cycloadditions in solid phase organic synthesis have appeared.⁷ The rich cycloaddition chemistry of mesoionic dipoles has been reviewed.⁸ Within [4 + 2] cycloaddition chemistry, Padwa has reviewed synthetic applications of furan Diels–Alder chemistry.⁹ The preparation and use of chiral sulfinyl 1,3-dienes has been described.¹⁰ Other reviews include new “designer” aluminium based Lewis acid catalysts,¹¹ enantioselective Diels–Alder reactions using metallocenes,¹² synthetic

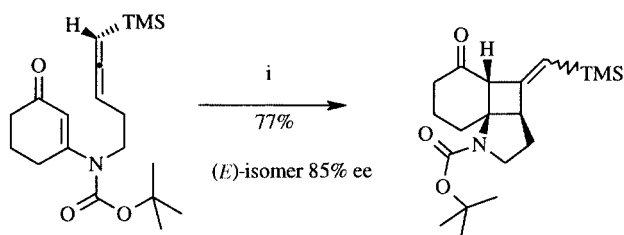
equivalents of cyclohexatriene,¹³ intramolecular reactions of temporarily silicon-tethered molecules,¹⁴ tandem Pummerer–Diels–Alder sequences,¹⁵ [4 + 2] routes to taxoids,¹⁶ activation of aromatic molecules with pentaammineosmium(II)¹⁷ and uses of camphor-derived alkenyloxazolines.¹⁸ Reviews on hetero-Diels–Alder chemistry include Tietze’s *tour de force*,¹⁹ new synthetic routes to nitrogen heterocycles²⁰ and the synthesis of pyrans.²¹ Rigby,²² Harmata²³ and Barbosa²⁴ have all reviewed the [4 + 3] cycloaddition area. Molybdenum-catalysed and -mediated [6 + 2] cycloadditions²⁵ and transition metal-assisted cycloadditions²⁶ have been the subject of other reviews. As well as reviewing [4 + 3] cycloaddition chemistry, Rigby has reviewed [6 + 4] cycloadditions.²⁷ The fourth volume of “*Advances in Cycloaddition*” has been published,²⁸ including sections on photoadditions of 2- and 4-pyrones, catalytic asymmetric [2 + 2] cycloadditions, Diels–Alder reactions of vinylboranes, cycloaddition reactions of cobaloxime substituted dienes and [4 + 3] cycloadditions. Finally *o*-benzoquinone cycloadditions have been reviewed.²⁹

2 [2 + 2] Cycloadditions

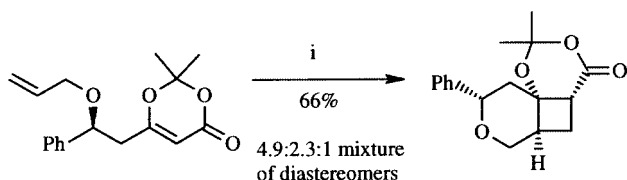
A number of research groups, including that of Carreira, have actively contributed to the area of [2 + 2]-intramolecular photocycloaddition chemistry. Particularly interesting examples involve the use of optically active allenes (Schemes 1, 2) and dioxinones (Schemes 3, 4) in enantioselective approaches to complex polycyclic compounds.^{30–33} Allenes have also been used in a new route to benzocyclobutenes (Scheme 5).³⁴ The use of chiral hydroxy acids as temporary spacers to allow enantioselective photocyclisation between allyl alcohol and 3-carboxycyclohexenone has been successfully demonstrated (Scheme 6).³⁵ Similarly, the use of a tartrate derived chiral auxiliary has been reported to allow asymmetric photodimerisations of cinnamate esters (Scheme 7).³⁶ Related diastereoselective cycloadditions of both cyclohexenones and cyclopentenones with a non-removable tether have been described by Crimmins^{37,38} and other workers.³⁹ Photochemical, Lewis acid-catalysed and ketene [2 + 2] cycloadditions have been used as approaches to natural product skeletons, including the terpenoid (\pm)-norasteriscanolide (Scheme 8),⁴⁰ new sesquiterpene frameworks (Scheme 9)⁴¹ and the furanoditerpene (+)-taonianone (Scheme 10).⁴² Palomo’s group has made a number of contributions to the asymmetric synthesis of β -lactams using the chiral Evans–Sjögren aminoketene, generated by dehydrochlorination of **1**, in reactions with imines.^{43–45} The methodology can be used to construct quaternary centres (Scheme 11).⁴⁵ Ketenes generated by Wolff rearrangement of diazo ketones derived from protected α -amino acids react with imines to yield β -lactams (Scheme 12).⁴⁶ Dimethylaluminium enolates undergo [2 + 2] cycloadditions with phenyl vinyl sulfoxide (Scheme 13).⁴⁷ Cycloaddition of ketenes to the (*R*)-2-*tert*-butyldihydrooxazole **2** unexpectedly leads to the cyclobutanone regioisomer **3** as the major product (Scheme 14).⁴⁸ Reaction of the ketene derived from 2-methylpropanoyl chloride with 4-nitrobenzaldehyde in 5 M lithium perchlorate–diethyl ether yields the oxetanone **4** (Scheme 15).⁴⁹ If 4-methoxybenzaldehyde is used instead, the product obtained is the styrene, generated by decarboxylation of the initially formed oxetanone. Cyclobutadienes, generated by



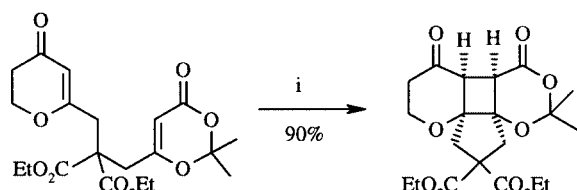
Scheme 1 Reagents and conditions: i, hv, CH₂Cl₂; TBS = *tert*-butyldimethylsilyl.



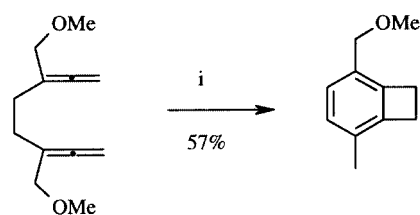
Scheme 2 Reagents and conditions: i, hv, C₆H₁₂.



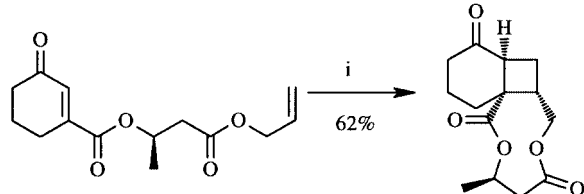
Scheme 3 Reagents and conditions: i, hv, 10% Me₂CO–MeCN.



Scheme 4 Reagents and conditions: i, hv, MeCN, 0 °C.

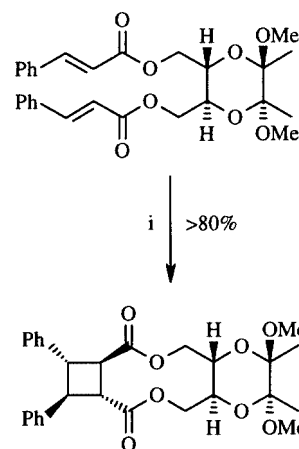


Scheme 5 Reagents and conditions: i, PhMe, Δ.

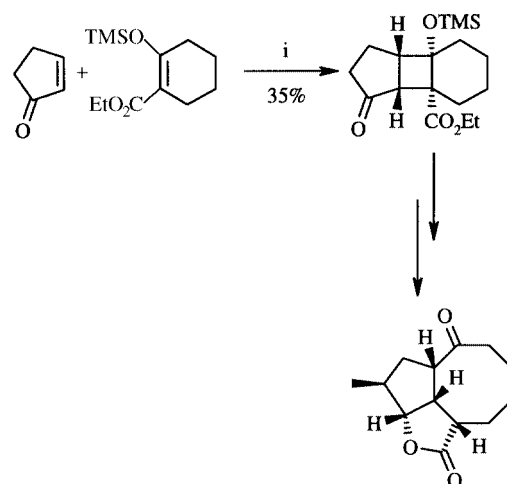


Scheme 6 Reagents and conditions: i, hv, CH₂Cl₂.

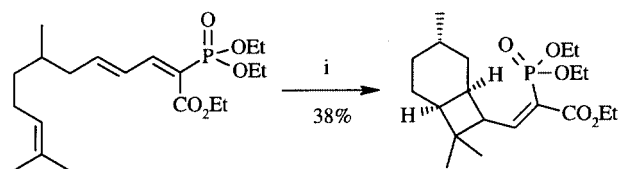
oxidation of tricarbonyl(η^4 -cyclobutadiene)iron complexes react in an intramolecular sense with unactivated alkenes (Scheme 16).⁵⁰ The selective excitation of the isolated crystalline charge transfer complex between acenaphthylene and tetracyanoethylene gives a [2 + 2] cycloadduct (Scheme 17).⁵¹ The reaction does not occur in solution or when an equimolar solid mixture of the two components is irradiated, dimerisation of the acenaphthylene occurring instead.



Scheme 7 Reagents and conditions: i, hv, PhMe, –60 °C.



Scheme 8 Reagents and conditions: i, hv, CH₂Cl₂.

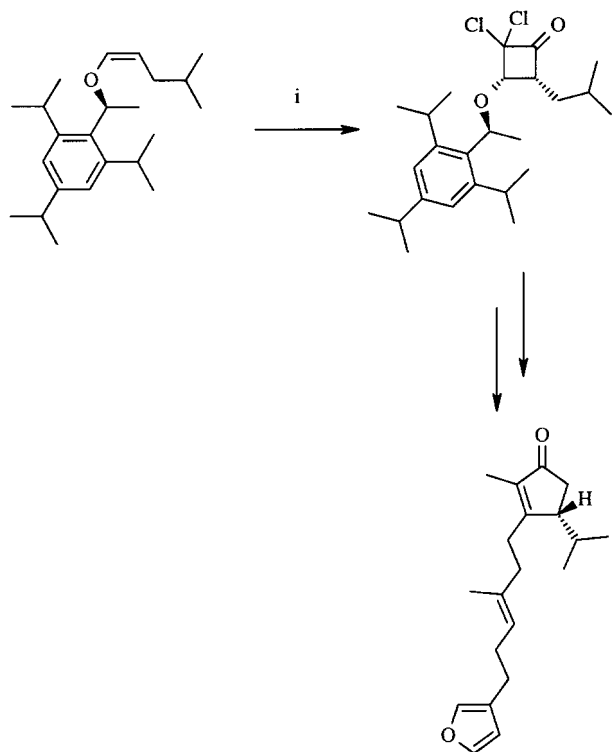


Scheme 9 Reagents: i, SnCl₄, Cl(CH₂)₂Cl.

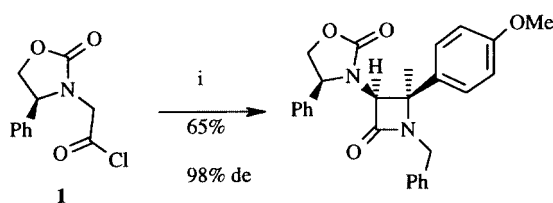
3 [3 + 2] Cycloadditions

3.1 Azomethine ylides

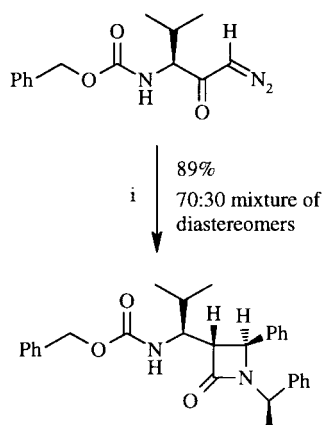
Gallagher and Hales have recently described a brief approach to penams and penems involving the cycloaddition of a thio-carbonyl compound with an azomethine ylide derived from the oxazolidinone **5** (Scheme 18).⁵² The reactive intermediate in the protocol has been suggested to be **6** rather than the anticipated **7**.⁵³ Harwood has extended the chemistry of (*5S*)-5-phenylmorpholin-2-one to the synthesis of enantiomerically pure 5-hydroxymethylprolines by sequential intramolecular [3 + 2] azomethine ylide cycloaddition–Pummerer rearrangement (Scheme 19).⁵⁴ A search to find an alternative to an aldehyde in the ylide forming step led to the identification of the *tert*-butyl carbamate **8** as a suitable substrate for generation of the azomethine species under mild conditions (Scheme 20).⁵⁵ A route to azomethine ylides and 2-azaallyl anions from a common precursor has been described by Pearson (Scheme 21).⁵⁶ The method can be carried out either by preparing and isolating the cycloaddition precursor or by a three-component *in situ* procedure.⁵⁶ The 2-azaallyl anion methodology can be extended to the solid phase synthesis of pyrrolidines.⁵⁷ Aziridines have been used by a number of groups to generate azomethine ylides



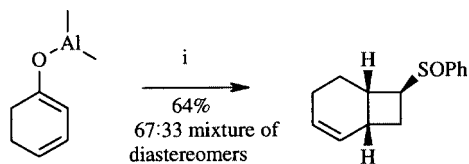
Scheme 10 Reagents: i, Cl_3CCOCl , Zn–Cu, Et_2O .



Scheme 11 Reagents and conditions: i, $\text{BnN}=\text{C}(\text{Me})(\text{PMP})$ (PMP = *p*-methoxyphenyl), NEt_3 , CHCl_3 , -78°C .

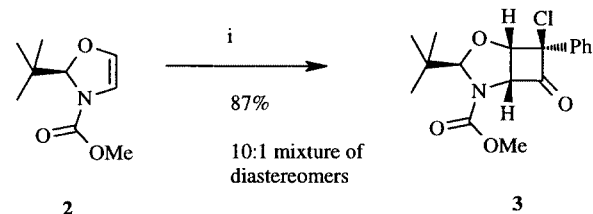


Scheme 12 Reagents and conditions: i, $\text{PhCH}=\text{NCH}(\text{Me})\text{Ph}$, $h\nu$, Et_2O , -15°C .

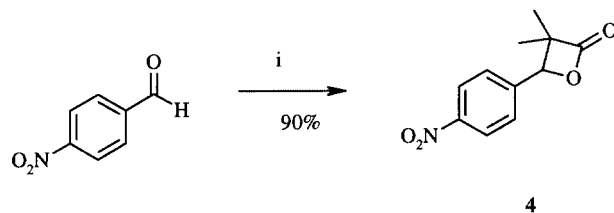


Scheme 13 Reagents and conditions: i, $\text{H}_2\text{C}=\text{CHS}(\text{O})\text{Ph}$, Et_2O –THF, -30°C .

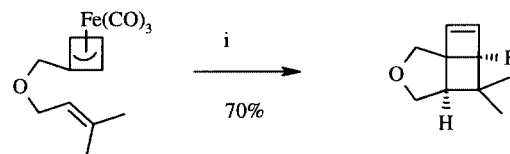
which then undergo [3 + 2] cycloadditions. Examples include the intramolecular photochemical reaction of the silicon-tethered acrylate **9** (Scheme 22)⁵⁸ and a photoinduced electron



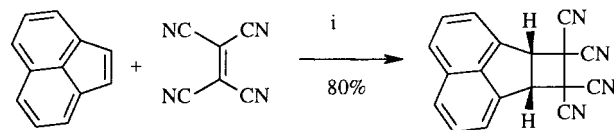
Scheme 14 Reagents and conditions: i, $\text{O}=\text{C}(\text{Cl})\text{Ph}$, C_6H_{12} , 60°C .



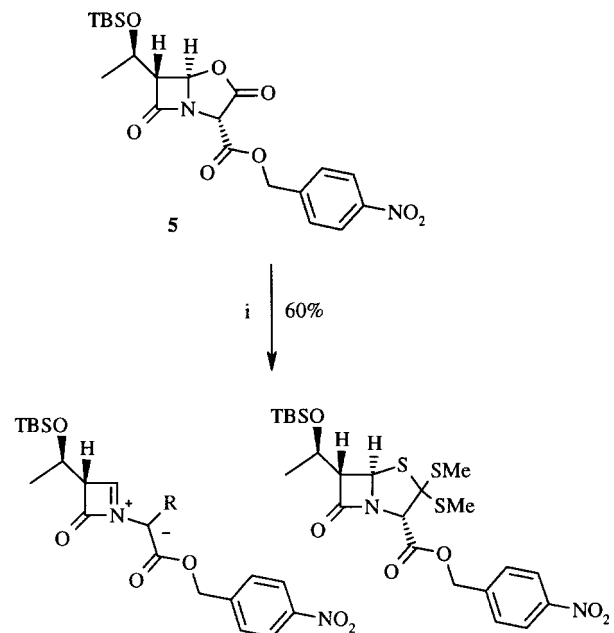
Scheme 15 Reagents: i, Me_2CHCOCl , NEt_3 , 5 M LiClO_4 – Et_2O .



Scheme 16 Reagents and conditions: i, CAN, Me_2CO , -5°C .



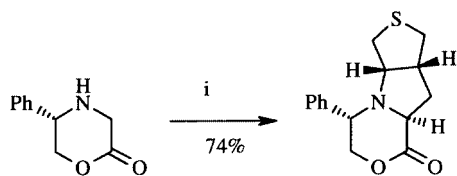
Scheme 17 Reagents and conditions: i, $h\nu$, crystal state.



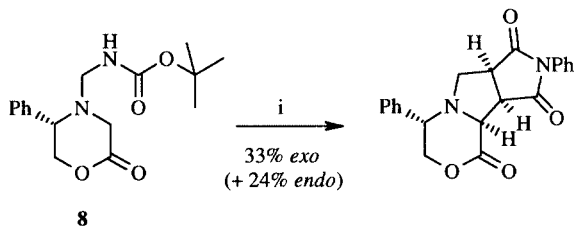
6 R = CO_2H ; **7** R = H

Scheme 18 Reagents and conditions: i, $(\text{MeS})_2\text{C}=\text{S}$, MeCN, Δ .

transfer reaction of **10** with dipolarophiles (Scheme 23).⁵⁹ Overman has used an elegant intramolecular azomethine ylide reaction with *in situ* generated enecarbamates as an approach to hexahydrotriquinacenes (Scheme 24).⁶⁰ Approaches to the stereocontrolled synthesis of polysubstituted pyrrolidines commonly involve azomethine ylides.^{61–63} The chemistry is applicable to pyrrolizidines,⁶⁴ spiro-fused compounds⁶⁵ and to solid phase synthesis.⁶⁶ Some examples include the synthesis of



Scheme 19 Reagents and conditions: i, $\text{H}_2\text{C}=\text{CHCH}_2\text{SCH}_2\text{CHO}$, PhMe, Δ .

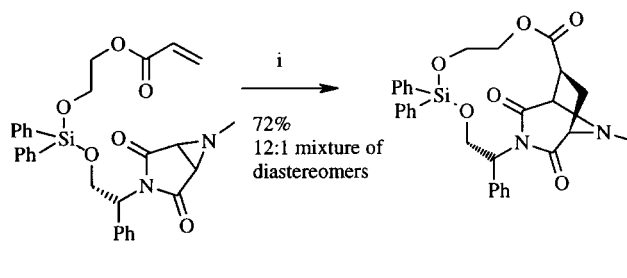


Scheme 20 Reagents: i, *N*-phenylmaleimide (NPM), TFA, THF.

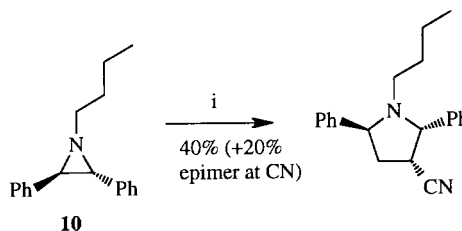
C_2 symmetric cycloadducts as precursors to new chiral auxiliaries (Scheme 25),⁶¹ and a brief approach to homochiral 2,3,4-trisubstituted pyrrolidines (Scheme 26).⁶² Samarium(III) azomethine ylides have been generated and used in a route to γ -carboxypyrrolidines (Scheme 27).⁶⁷ Enantiopure sulfinimines undergo asymmetric dipolar cycloadditions with azomethine ylides producing imidazolines (Scheme 28).⁶⁸ In related chemistry 2-aryl pyrrolidines are prepared by the cycloaddition of lithiated sulfones to sulfinimines.⁶⁹ Ylides derived from pyrazinium⁷⁰ and dihydroisoquinolinium⁷¹ species have yielded routes to novel fused heterocycles (Scheme 29) and to the natural product lamellarin K (Scheme 30).

3.2 Nitrones

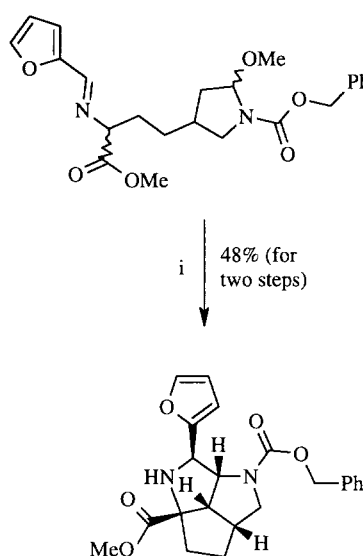
The novel homochiral cyclic nitron **11** has been designed using judicious positioning of substituents to achieve maximal π -facial bias for both nitron and dipolarophile.⁷² This is the first nitron reportedly to be able to exercise complete facial discrimination within geometric isomers of 1,2-di- and 1,1,2-trisubstituted alkenes, thus cycloadduct **12** is the exclusive product from the reaction with dimethyl α -methylfumarate (Scheme 31).⁷² The optically pure nitron **13** has been used in a highly *endo* selective cycloaddition with vinylene carbonate providing a key intermediate for the synthesis of the carbohydrate portion of the antifungal agent Sch 38516 (Scheme 32).⁷³ A spironitron **14** reacts with a cyclic allylic silane to provide a route to (2*S*,1'*S*)- α -(cyclopent-2-enyl)glycine (Scheme 33).^{74,75} The homochiral geometry fixed nitron **15** has also been used successfully in reactions with alkenes and vinyl ethers.⁷⁶ A one step preparation has been used to generate (*S*)-5-hydroxymethyl-1-pyrroline-*N*-oxide, a homochiral nitron that reacts with complete diastereofacial differentiation with a number of electron-deficient alkenes.⁷⁷ Camphor derived oxazoline *N*-oxides have been used to generate a wide variety of enantiomerically pure compounds.¹⁸ A number of groups have examined asymmetric approaches to isoxazolidines using nitrones and chiral catalysts (Scheme 34), including lanthanide triflates plus chiral



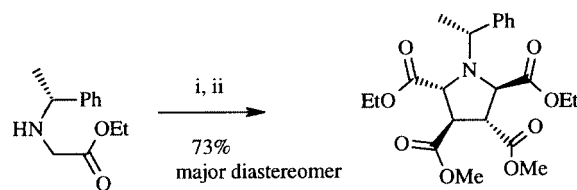
Scheme 22 Reagents and conditions: i, hv, MeCN.



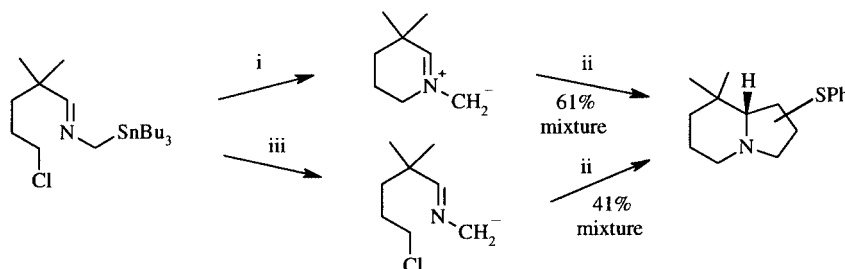
Scheme 23 Reagents and conditions: i, $\text{H}_2\text{C}=\text{CHCN}$, hv, MeCN.



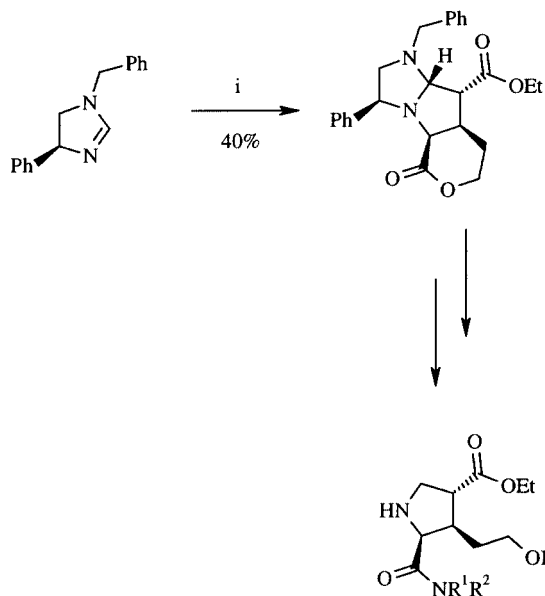
Scheme 24 Reagents and conditions: i, NH_4Cl , xylene, Δ .



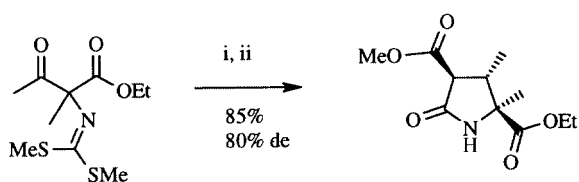
Scheme 25 Reagents and conditions: i, EtO_2CCHO , PhMe, Δ ; ii, $\text{MeO}_2\text{CCH}=\text{CHCO}_2\text{Me}$.



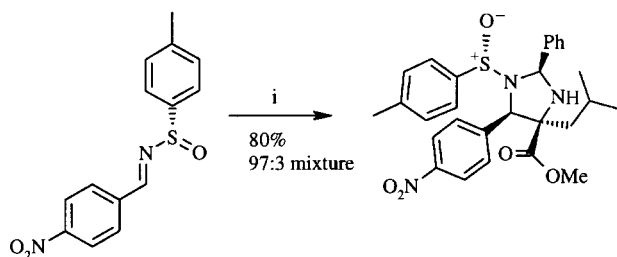
Scheme 21 Reagents and conditions: i, PhMe, Δ ; ii, $\text{PhSCH}=\text{CH}_2$; iii, Bu^nLi .



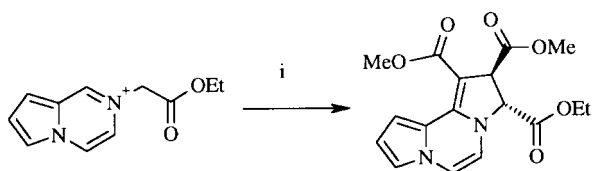
Scheme 26 Reagents and conditions: i, $\text{BrCH}_2\text{CO}_2(\text{CH}_2)_2\text{CH}=\text{CH}-\text{CO}_2\text{Et}$, DBU, THF, Δ .



Scheme 27 Reagents and conditions: i, $\text{MeCH}=\text{CHCO}_2\text{Me}$, SmI_2 , THF; ii, 1 M HCl.

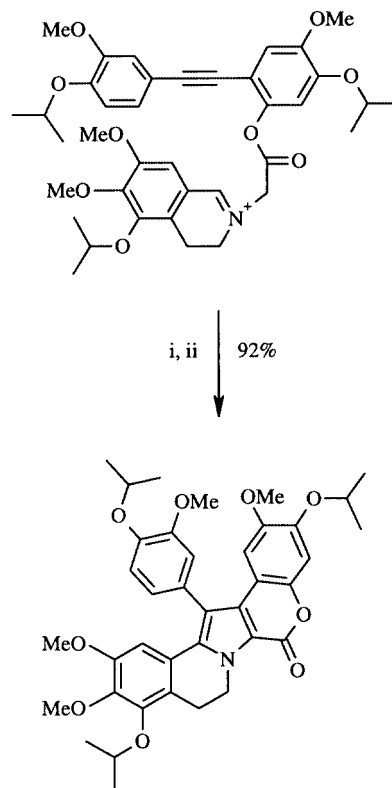


Scheme 28 Reagents and conditions: i, $\text{Li}^+[\text{PhCH}=\text{NC}(\text{Bu}^t)\text{CO}_2\text{Me}]^-$, THF, -78°C .

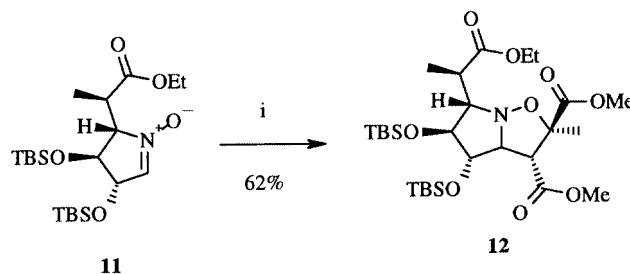


Scheme 29 Reagents: i, DMAD, CH_2Cl_2 , aq. K_2CO_3 .

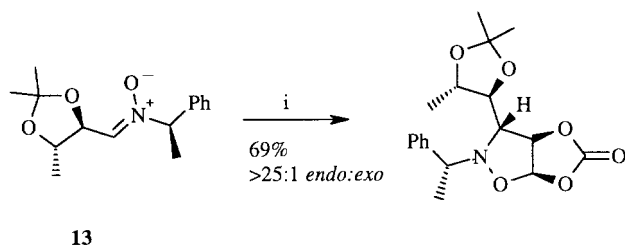
ligands,^{78,79} TiCl_2 -TADDOLates,⁸⁰ including novel polymer and dendrimer-bound titanium TADDOLates,⁸¹ and chiral palladium phosphine complexes.⁸² Jørgensen has found that substitution of the traditional crotonoyl oxazolidinone moiety with the succinimide **16** leads to improved diastereoselectivities, and enantioselectivities, in TiCl_2 -TADDOLate catalysed [3 + 2] cycloadditions with nitrones, especially when the titanium TADDOLate **17** is used.⁸³ Koskinen has reported the use of an acrylamide bearing Oppolzer's chiral sultam in a nitron approach to enantiopure γ -hydroxyglutamates.⁸⁴ Using chiral oxazaborolidine catalysts derived from *N*-arylsulfonyl protected *L*-amino acids and borane-THF complex, vinyl ethers react with nitrones with only very modest enantioselectivity.^{85,86} More successful is the use of vinyl ethers (e.g. **18**) or



Scheme 30 Reagents and conditions: i, NEt_3 , THF, Δ ; ii, DDQ, CH_2Cl_2 .

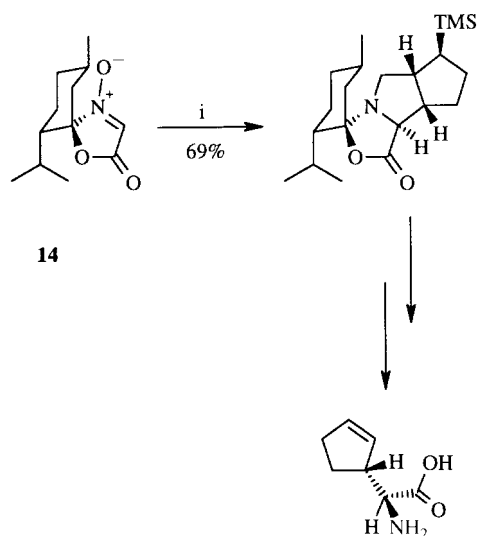


Scheme 31 Reagents and conditions: i, (*E*)-dimethyl α -methylfumarate, PhH, Δ .

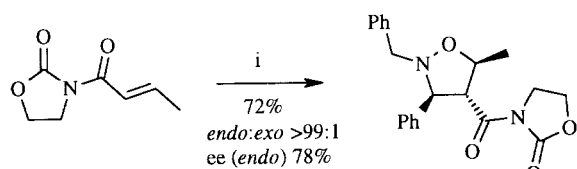
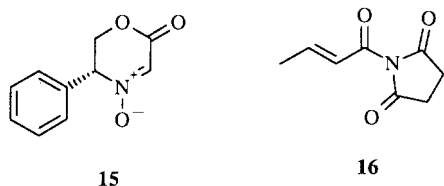


Scheme 32 Reagents and conditions: i, vinylene carbonate, C_6H_6 , Δ .

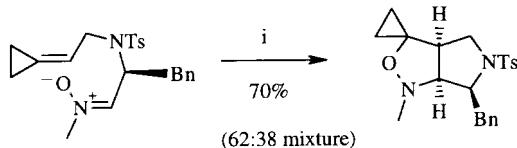
alkenes bearing a chiral sulfoxide group.^{87,88} Introduction of a 2-fluoro substituent into a nitron is reported to influence the diastereoselectivity of reactions with ethyl vinyl ether.⁸⁹ Examples of intramolecular reactions include the use of optically pure amino acid derived alkydenecyclopropane species (Scheme 35),⁹⁰ an approach to enantiopure 4-amino-chromanes,⁹¹ a synthesis of (-)-shikimic acid,⁹² the use of sulfolene generated dienes (Scheme 36)⁹³ and a cascade nitron formation, transesterification, *E/Z* isomerisation and stereocontrolled cycloaddition to yield the *N*-terminal amino acid component of nikkomycin Bz (Scheme 37).⁹⁴ Grigg has continued to provide the driving force behind the development of complex cascade reactions⁹⁵⁻⁹⁷ with a typical example yielding an enantiopure cycloadduct being shown in Scheme 38.⁹⁷ Miscellaneous other examples of cycloadditions involving nitrones



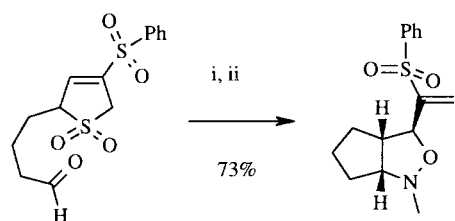
Scheme 33 Reagents: i, 3-(trimethylsilyl)cyclopent-1-ene, $\text{BF}_3 \cdot \text{OEt}_2$, MeCN.



Scheme 34 Reagents: i, $\text{PhCH}=\text{N}^+(\text{O}^-)\text{Bn}$, Yb^* , CH_2Cl_2 .

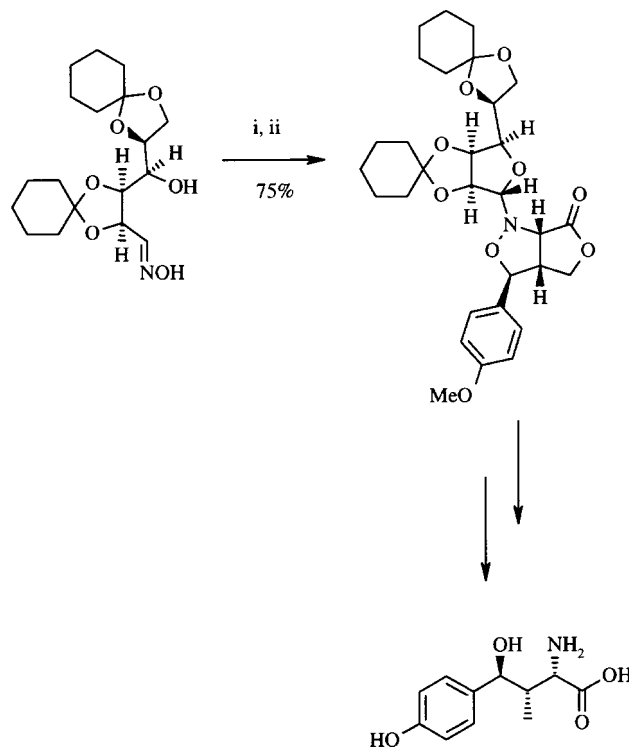


Scheme 35 Reagents: i, Et_2O , pyridine.

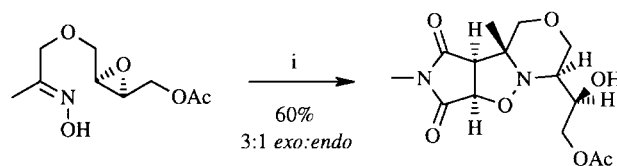


Scheme 36 Reagents and conditions: i, $\text{MeNH}_2 \cdot \text{HCl}$, NaOMe, PhMe, rt; ii, PhMe, Δ .

include reactions with α -methylene β -lactams generating novel spiro compounds,^{98,99} microwave acceleration of the cycloaddition,¹⁰⁰ addition to unsaturated boranes,¹⁰¹ addition to

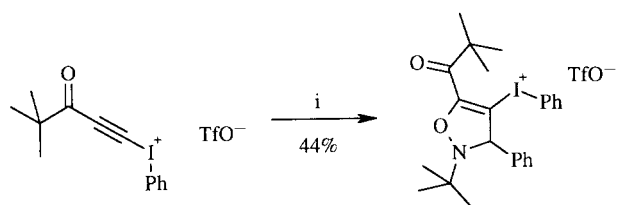


Scheme 37 Reagents and conditions: i, $\text{MeOCH}(\text{OH})\text{CO}_2\text{Me}$, PhMe, Δ ; ii, (*E*)-*p*- $\text{MeOC}_6\text{H}_4\text{CH}=\text{CHCH}_2\text{OH}$, TiCl_4 , 100 °C.

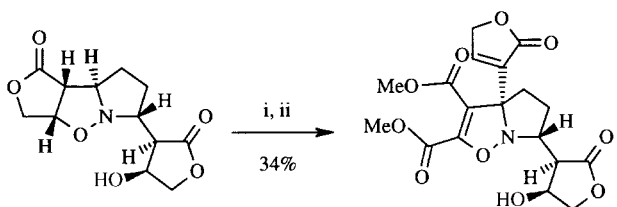


Scheme 38 Reagents and conditions: i, NMM, EtOH, Δ .

alkynyl(phenyl)iodonium triflates (Scheme 39)¹⁰² and the first example of a “third generation” nitronate cycloaddition (Scheme 40).¹⁰³



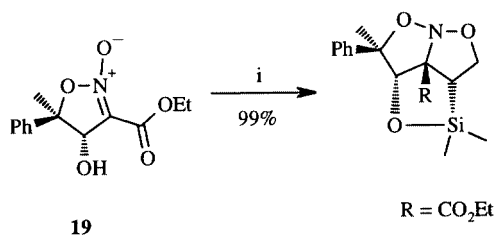
Scheme 39 Reagents: i, $\text{PhCH}=\text{N}^+(\text{O}^-)\text{Bu}^t$, CH_2Cl_2 .



Scheme 40 Reagents: i, *m*-CPBA, CH_2Cl_2 , 0 °C; ii, DMAD, CH_2Cl_2 .

3.3 Nitronates

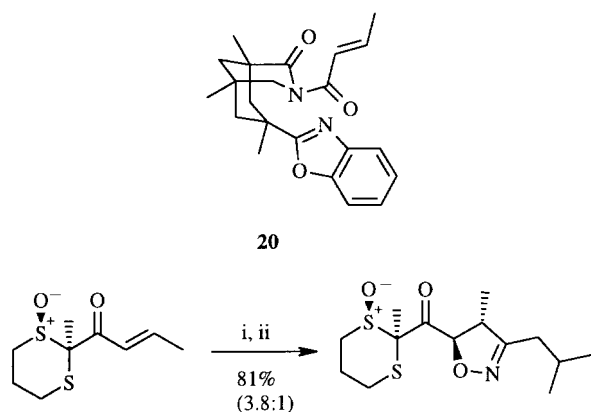
A number of groups have reported on the reactions of silyl nitronates, examples include reactions with homochiral enones¹⁰⁴ and diastereoselective intramolecular cycloadditions.^{105,106} The use of a silicon tether in a cycloaddition involving the racemic nitronate **19** has also been described (Scheme 41).¹⁰⁷



Scheme 41 Reagents: i, H₂C=CHSiMe₂Cl, imidazole, MeCN.

3.4 Nitrile oxides

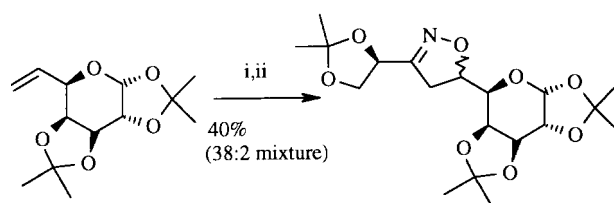
A new, mild procedure for the *in situ* generation of nitrile oxides from nitroalkanes using di-*tert*-butyl dicarbonate and DMAP has been published.¹⁰⁸ Alternative reagents for this dehydration include the Burgess reagent, DAST, acetic anhydride, oxalyl chloride and phosphorus oxychloride (all used with triethylamine).¹⁰⁹ Reagents such as DCC, thionyl chloride, triflic anhydride, triphenylphosphine oxide/triflic anhydride, Mukaiyama's reagent and butyltin oxide reportedly failed.¹⁰⁹ Dehydrohalogenation of hydroximoyl chlorides is a popular route to nitrile oxides—Kulkarni has generated a new route to the precursor hydroximoyl chlorides by reacting titanium tetrachloride with nitroalkenes.¹¹⁰ The regiochemistry of cycloaddition of a nitrile oxide to a terminal alkene can be reversed by tethering the olefin to a β -cyclodextrin.¹¹¹ Conducting nitrile oxide cycloadditions under microwave irradiation in the absence of solvent reportedly results in yield improvement and dramatic reduction in reaction time.¹¹² Protection of 2-oxopropanenitrile oxide as its 1,3-dithiane reportedly reduces the competing dimerisation often seen with alkyl nitrile oxides.¹¹³ Reactions of acryloyl derivatives (*e.g.* **20**) of the Rebek imide benzoxazole chiral auxiliary with nitrile oxides have been studied.¹¹⁴ Page has described regioselective and stereoselective reactions of nitrile oxides with 2-alkenoyl-1,3-dithiane-1-oxides (Scheme 42).¹¹⁵ Interestingly, the same authors report that the addition of Lewis acids can alter or even reverse the stereoselectivity of these 1,3-dipolar cycloadditions.¹¹⁶ Nitrile oxides have been used in approaches to higher monosaccharides (Scheme 43),¹¹⁷ to a potential intermediate for the alkaloid papuamine,¹¹⁸ to the CDE fragment of the insect antifeedant 12-hydroxyazadiradione,¹¹⁹ to diaminohexanes as building blocks for HIV protease inhibitors (Scheme 44)¹²⁰ and in an enantioselective total synthesis of (+)-cassiol (Scheme 45).¹²¹



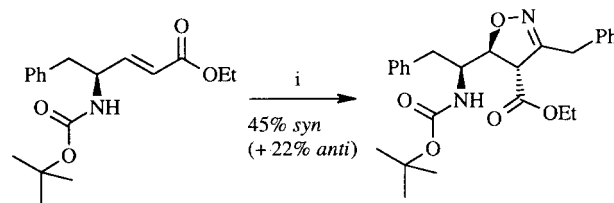
Scheme 42 Reagents: i, NEt₃, Et₂O; ii, Me₂CHCH₂C(Cl)=NOH.

3.5 Carbonyl ylides and isomünchnones

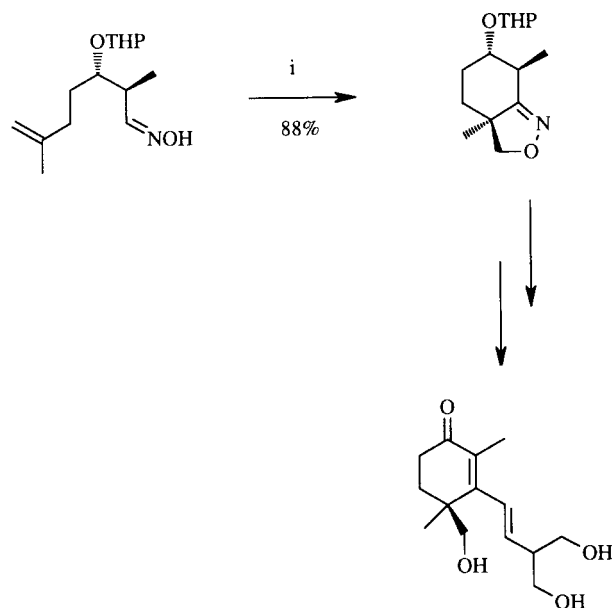
Padwa has published extensively on the use of carbonyl ylide dipoles in cycloaddition reactions. He has investigated many different aspects of the reaction, including cyclisation of rhodium carbenoids onto ester and amide carbonyls (Scheme 46),¹²² the π -facial diastereoselection of the reaction,¹²³ Pummerer reactions of imido sulfoxides in the generation of novel



Scheme 43 Reagents: i, NEt₃, Et₂O; ii, R^{*}C(Cl)=NOH.



Scheme 44 Reagents and conditions: i, Ph(CH₂)₂NO₂, PhNCO, NEt₃, PhH, Δ .

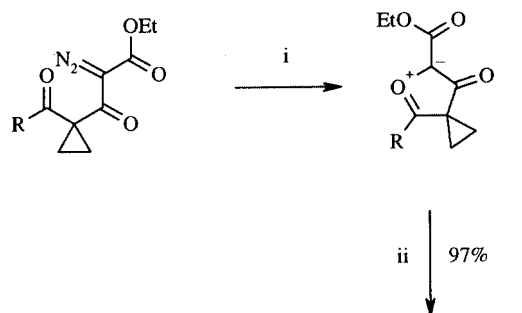


Scheme 45 Reagents: i, NaOCl, CH₂Cl₂.

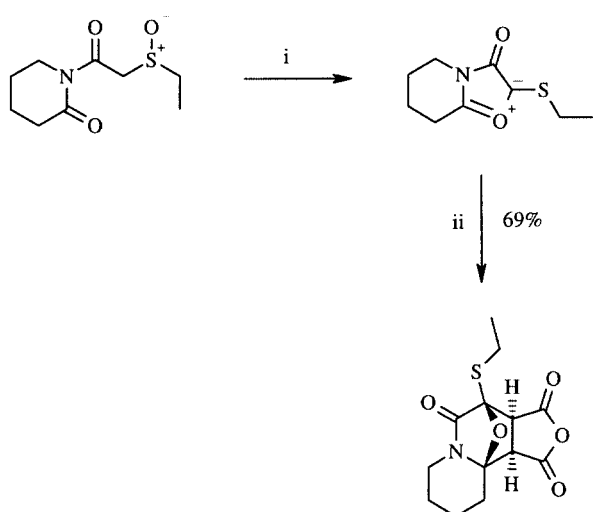
dipoles (Scheme 47),¹²⁴ including a tandem Pummerer–isomünchnone sequence to (\pm)-pumiliotoxin C,¹²⁵ a tandem cycloaddition–cationic π -cyclisation approach to (\pm)-lycopolidine,¹²⁶ a tandem cycloaddition–Mannich cyclisation route to nitrogen tricycles,¹²⁷ a new route to pyridones and thence to (\pm)-ipalbidine¹²⁸ and a route to the illudin sesquiterpenes.¹²⁹ Other workers have also used Padwa's approach to the illudins to prepare novel antitumour agents.^{130–132} A new route to carbonyl ylides involving the reaction of samarium reagents with α -chloroalkyl α' -chloroalkyl ethers has been reported.¹³³ Laser irradiation of aryl vinyl ethers also produces carbonyl ylides (Scheme 48).¹³⁴ Harwood has investigated the use of homo-chiral oxazine-2,3-diones¹³⁵ and oxazin-3-ones (Scheme 49)¹³⁶ as chiral templates in the reaction. Diastereofacial control here is surprisingly modest. A catalytic enantioselective variant of the cycloaddition using a rhodium *N*-[(4-dodecylphenyl)sulfonyl]proline catalyst has been described.¹³⁷ Two groups have described solid phase synthesis of combinatorial libraries of functionalised furans using an isomünchnone cycloaddition–cycloreversion sequence (Scheme 50).^{138,139}

3.6 Miscellaneous

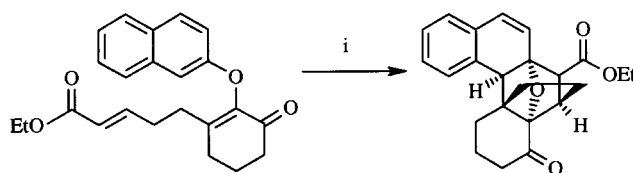
Trost has used his extensively developed TMM (trimethylene-methane)palladium chemistry in an asymmetric synthesis of



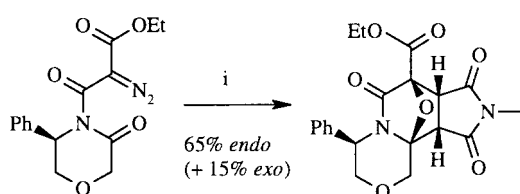
Scheme 46 Reagents: i, Rh^{II}; ii, DMAD.



Scheme 47 Reagents and conditions: i, PhMe, Ac₂O, *p*-TSA (cat.), Δ; ii, maleic anhydride.

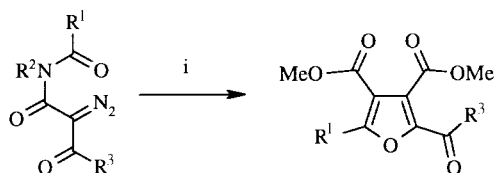


Scheme 48 Reagents and conditions: i, hv.

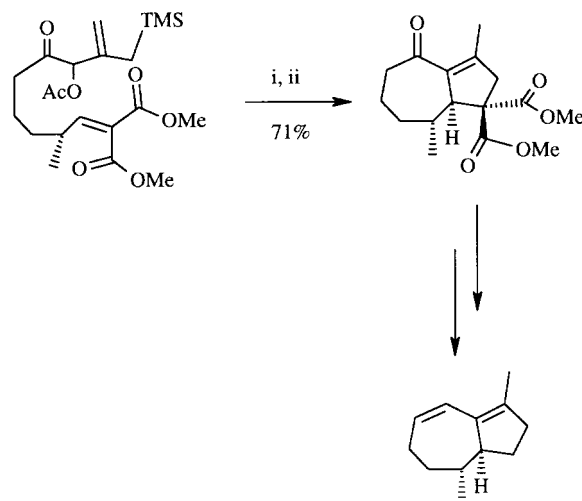


Scheme 49 Reagents and conditions: i, *N*-methylmaleimide (NMM), Rh₂(OAc)₄ (cat.), PhH, Δ.

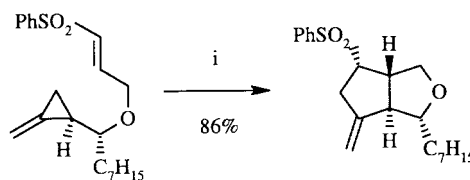
(-)-isoclavukerin A (Scheme 51).¹⁴⁰ Lautens' use of palladium catalysed reactions has extended to intramolecular cycloadditions of methylenecyclopropanes with electron-deficient alkenes (Scheme 52)¹⁴¹ and alkynes.¹⁴² Methylenecyclopentane generation *via* Lewis acid catalysed reactions of 1-alkylthio-2-(trimethylsilylmethyl)allyl esters with enol ethers and vinyl sulfides offers an attractive route to functionalised bicycles



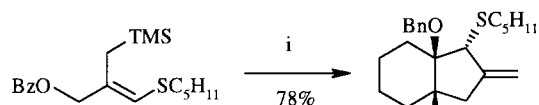
Scheme 50 Reagents and conditions: i, DMAD, Rh₂(OAc)₄ (cat.), PhH, Δ.



Scheme 51 Reagents and conditions: i, Pd(OAc)₂, (PrⁱO)₃P, Me₃-SnOAc, PhMe, Δ; ii, DBU, PhMe, 90 °C.



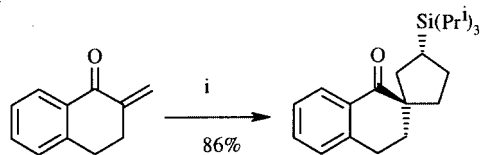
Scheme 52 Reagents and conditions: i, Pd(PPh₃)₄, PhMe, Δ.



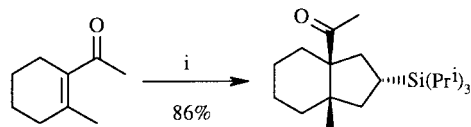
Scheme 53 Reagents and conditions: i, 1-Benzyloxycyclohex-1-ene, MeAl(OTf)₂, CH₂Cl₂, -23 °C.

(Scheme 53).¹⁴³ Knölker has developed his Lewis acid catalysed cycloaddition of allylsilanes with olefins to the diastereoselective synthesis of spirocyclopentanes (Scheme 54)¹⁴⁴ and to the synthesis of bicyclo[*n*.3.0]alkanes, including the facility to generate two contiguous quaternary carbon centres (Scheme 55).¹⁴⁵ Asymmetric cycloadditions of (trimethylsilyl)diazomethane to acrylamides have yielded enantioselective routes to azaproline¹⁴⁶ and to *ent*-stelletamide A (Scheme 56).¹⁴⁷ Barluenga describes the diastereoselective addition of (trimethylsilyl)diazomethane to (-)-8-phenylmenthol derived pentacarbonylalkenyl(alkoxy)chromium carbene complexes (Scheme 57).¹⁴⁸ Diazomethane reportedly adds in an asymmetric fashion to homochiral vinyl sulfoxides (Scheme 58).¹⁴⁹ Huisgen continues steadfastly to examine the chemistry of sulfines^{150–152} and thiosulfines.¹⁵³ A sulfine example is shown (Scheme 59).¹⁵⁰ A variety of other [3 + 2] cycloadditions involving quinazolone ylides (Scheme 60),¹⁵⁴ phthalazinium methanides,¹⁵⁵ nitrilimines (Scheme 61),¹⁵⁶ intermolecular (Scheme 62)¹⁵⁷ and intramolecular (Scheme 63)¹⁵⁸ azomethine imine cycloadditions have been published. The addition of catalytic quantities of triphenylphosphine to allene esters generates a dipole which then can undergo cycloaddition to tosyl imines to produce

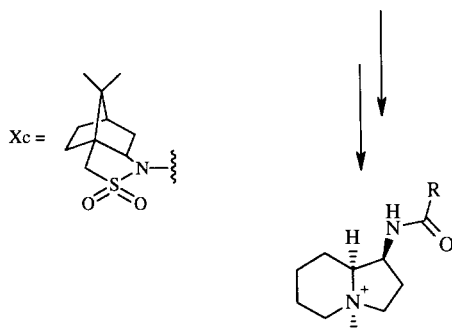
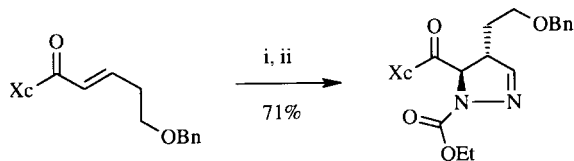
nitrogen heterocycles (Scheme 64).¹⁵⁹ This chemistry has also provided a route to novel, optically active, constrained glutamate analogues (Scheme 65).¹⁶⁰



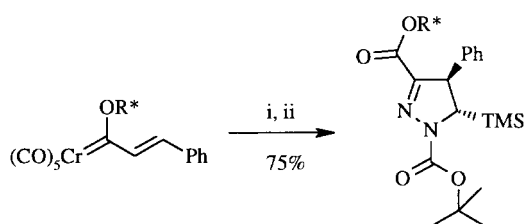
Scheme 54 Reagents and conditions: i, $\text{H}_2\text{C}=\text{CHCH}_2\text{Si}(\text{Pr}^i)_3$, TiCl_4 , CH_2Cl_2 , -78°C .



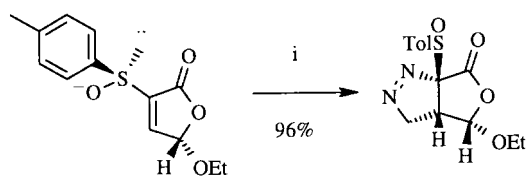
Scheme 55 Reagents and conditions: i, $\text{H}_2\text{C}=\text{CHCH}_2\text{Si}(\text{Pr}^i)_3$, TiCl_4 , CH_2Cl_2 , -78°C .



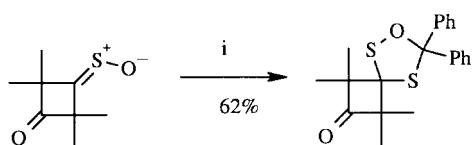
Scheme 56 Reagents: i, TMSCHN_2 , hexane- CH_2Cl_2 ; ii, EtOCOCl , AgOTf .



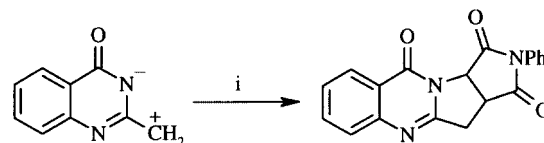
Scheme 57 Reagents and conditions: i, TMSCHN_2 , THF, -78°C ; ii, Boc_2O , NEt_3 , DMAP, THF, -78°C .



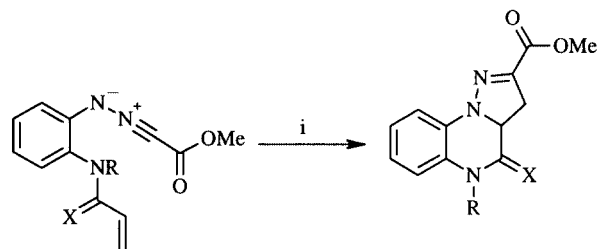
Scheme 58 Reagents and conditions: i, CH_2N_2 , Et_2O , 0°C .



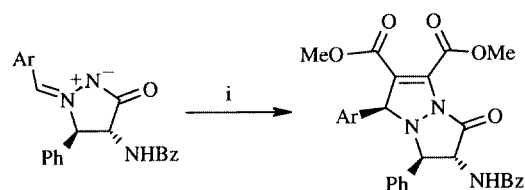
Scheme 59 Reagents: i, $\text{Ph}_2\text{C}=\text{S}$, pentane- CH_2Cl_2 .



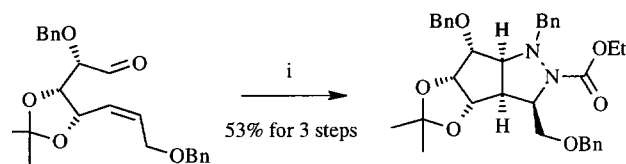
Scheme 60 Reagents: i, NPM, CHCl_3 .



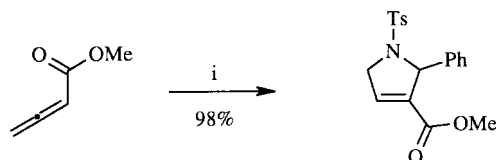
Scheme 61 Reagents and conditions: i, PhH, Δ .



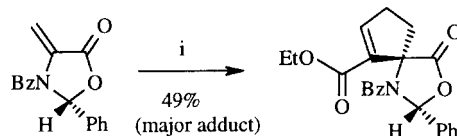
Scheme 62 Reagents and conditions: i, DMAD, PhOMe, Δ .



Scheme 63 Reagents and conditions: i, $\text{BnNHNHCO}_2\text{Et}$, NEt_3 , PhMe, Δ .



Scheme 64 Reagents: i, $\text{PhCH}=\text{NTs}$, Ph_3P , PhH.



Scheme 65 Reagents: i, $\text{H}_2\text{C}=\text{C}=\text{CHCO}_2\text{Et}$, Ph_3P , PhH.

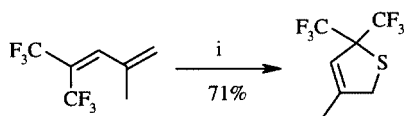
4 [4 + 1] Cycloadditions

Elemental sulfur and selenium reportedly add to trifluoromethyl substituted dienes, yielding dihydrothiophenes and dihydroselenophenes respectively (Scheme 66).¹⁶¹ The use of a rhodium catalyst bearing chiral diphosphine ligands has allowed the development of an asymmetric [4 + 1] route to alkylidene cyclopentenones (Scheme 67).¹⁶² Enantiomeric excesses are in the 40–65% range. The use of increased pressure (5–15 atm) of carbon monoxide suppressed the competitive formation of the unwanted triene 21.

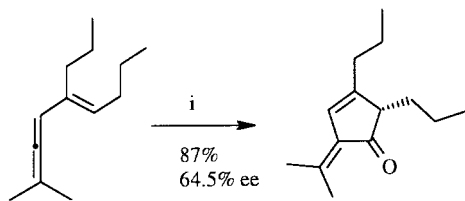
5 [4 + 2] Cycloadditions

5.1 General

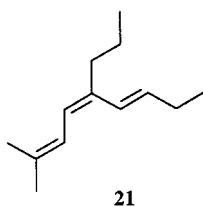
The synthetic applications of furan Diels–Alder chemistry has



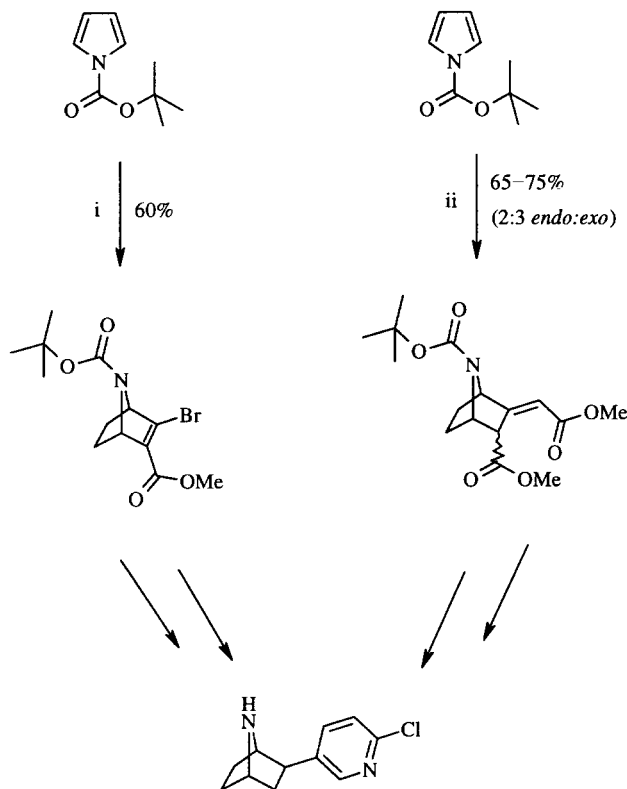
Scheme 66 Reagents and conditions: i, S₈, hydroquinone, TFAA (cat.), autoclave, 275 °C.



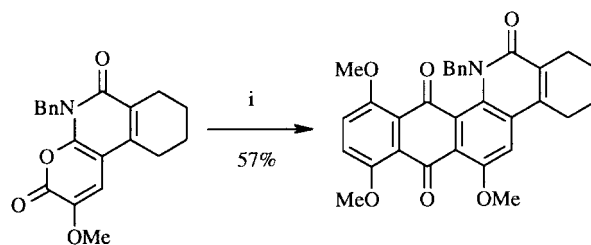
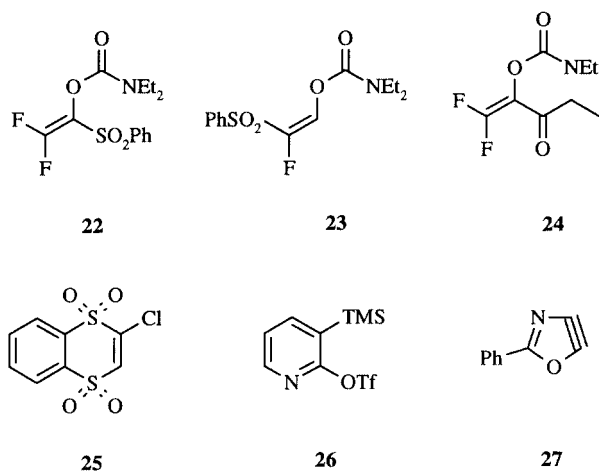
Scheme 67 Reagents and conditions: i, Rh[(R,R)-Me-DuPHOS](cod)-PF₆ (DuPHOS = 1,2-bis(2,5-dialkylphospholano)benzene), 5 atm CO, DME, 55–60 °C.



been the subject of a review by Padwa.⁹ The use of 2-amino-furans,¹⁶³ 3,4-diarylfurans¹⁶⁴ or 3,4-diarylthiophenes,¹⁶⁴ thiophene *S*-oxides¹⁶⁵ and various methoxythiophenes¹⁶⁶ in novel Diels–Alder approaches to anilines, methyl benzoates and dimethyl phthalates have also been published. Trudell has reported two approaches to the synthesis of the alkaloid (±)-epibatidine using [4 + 2] cycloadditions of *N*-acylpyrroles with methyl 3-bromopropiolate¹⁶⁷ and also with allene-1,3-diesters (Scheme 68).¹⁶⁸ A range of β-fluorinated dienophiles, for example **22–24**, and their reactions with cyclic and acyclic dienes have been described by Percy.^{169–171} Reactions of these novel dienophiles with cyclopentadiene are fine but reactions with furan either proceed in poor yield or not at all. The heterocycle 2-chloro-1,4-benzodithiine-*S,S'*-tetroxide **25** functions as a new synthetic equivalent for benzyne.¹⁷² Reactions between pyrones and benzyne give viable approaches to naphthalenes¹⁷³ and to the core ring system of dynemicin A (Scheme 69).¹⁷⁴ Annelated carbazoles can be prepared from 3-vinylindoles and benzyne,¹⁷⁵ but reactions with 3,4-pyridyne failed to generate the desired products. A mild process for the generation of 2,3-pyridyne involves treatment of **26** with caesium fluoride.¹⁷⁶ The [4 + 2] cycloadditions of a 4-nitrooxazole as the 2π component and its synthetic equivalence to the heteroaryne **27** represent a new dimension in oxazole chemistry (Scheme 70).¹⁷⁷ The existence of 3,4-didehydrothiophene has been substantiated by trapping experiments with alkenes.¹⁷⁸ Similarly, the cyclic butatriene cycloocta-1,2,3-triene has been generated for the first time and trapped with diphenylisobenzofuran.¹⁷⁹ A number of groups have experimented with cycloadditions of amino substituted butadienes. Thus Rawal (Scheme 71),¹⁸⁰ Pitacco (Scheme 72),¹⁸¹ Marchand–Brynaert (Scheme 73),¹⁸² Barluenga (Scheme 74),¹⁸³ Neier (Scheme 75),¹⁸⁴ Beifuss (routes to acridine and thioxanthenes)¹⁸⁵ and Hird (solid phase synthesis of 3,4,5-trisubstituted cyclohexanones)¹⁸⁶ have all made notable contributions. Boron substituted alkenes (Scheme 76),¹⁸⁷ dienylboronates (Scheme 77)^{188,189} and dienylboronate salts¹⁹⁰ have also proved to be useful synthetic building blocks. New iron tricarbonyl complexes of cross-conjugated polyenones undergo reactions with dienes, the major adduct being from cycloaddition to the face *anti* to the iron moiety (Scheme 78).¹⁹¹ Vinylallenes react with butadienes under palladium catalysis yielding cyclohexenes (Scheme 79).¹⁹² The reaction of alkynylidonium salts with dienes produces adducts bear-

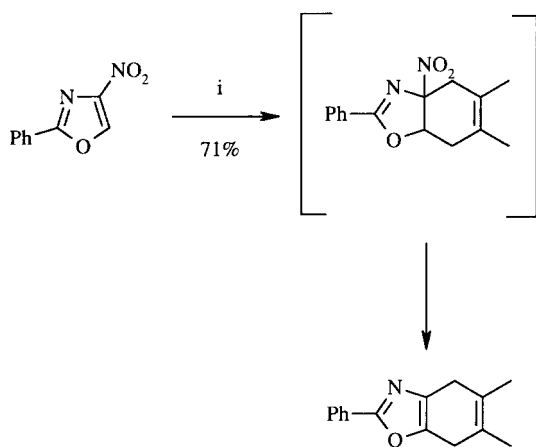


Scheme 68 Reagents and conditions: i, BrC≡CCO₂Me, 90 °C; ii, MeO₂CCH=C=CHCO₂Me, 85–90 °C.

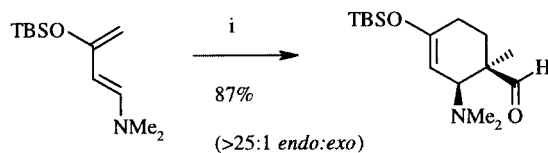


Scheme 69 Reagents: i, 5,8-dimethoxynaphthoquinone.

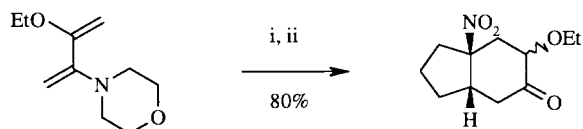
ing the vinyl(phenyl)iodonium functionality, a well-described vinyl cation equivalent.¹⁹³ Other polar cycloaddition reactions include those of 1-benzothiopyrylium salts (Scheme 80)^{194,195} and of butadienylpyridinium salts such as **30**.¹⁹⁶ Metal bearing dienes such as 3-methylene-2-ferrocenylmethylenequinuclidine,^{197,198} 2-cobaloxime substituted dienes (e.g. **31**)¹⁹⁹ and 4,5-η² osmium(II)pentammine 3-vinylpyrroles²⁰⁰ all successfully undergo [4 + 2] cycloaddition reactions.



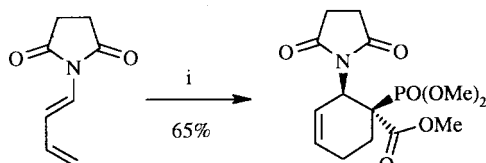
Scheme 70 Reagents and conditions: i, 2,3-dimethylbutadiene, CHCl_3 , 110°C .



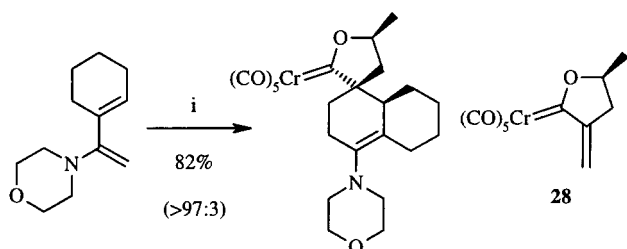
Scheme 71 Reagents: i, $\text{H}_2\text{C}=\text{C}(\text{Me})\text{CHO}$, PhMe .



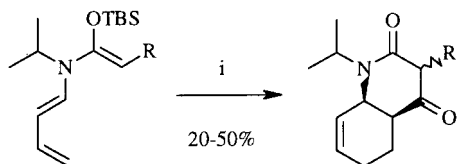
Scheme 72 Reagents: i, 1-nitrocyclopentene, PhMe ; ii, aq. HCl .



Scheme 73 Reagents and conditions: i, $\text{H}_2\text{C}=\text{C}(\text{CO}_2\text{Me})\text{PO}(\text{OMe})_2$, MeCN , 65°C .



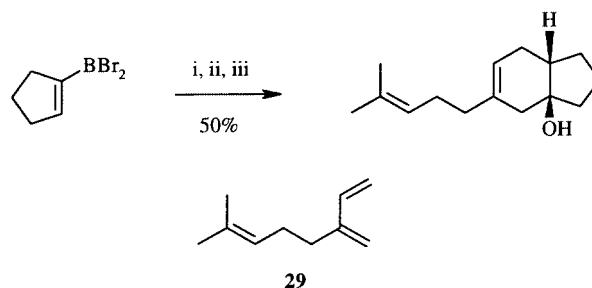
Scheme 74 Reagents and conditions: i, **28**, THF , -78°C .



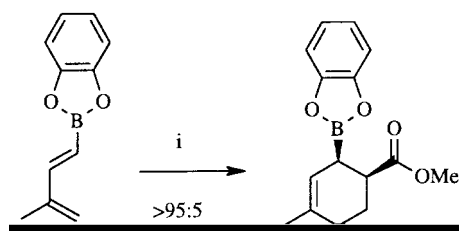
Scheme 75 Reagents and conditions: i, $\text{H}_2\text{C}=\text{CHCOCl}$, THF , -78°C ; ii, MeOH .

5.2 Methods of rate acceleration

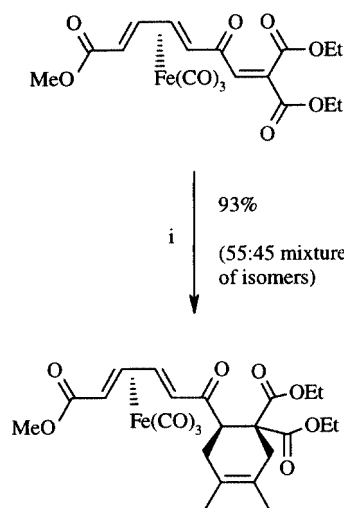
Lewis acid catalysis enables Diels–Alder reactions of the notoriously unreactive acyclic (*Z*)-1,3-dienes to occur successfully with, in most cases, excellent regio- and stereo-selectivity.²⁰¹ Methylalumoxane ($-\text{Al}[\text{Me}]_3$)²⁰² and other new



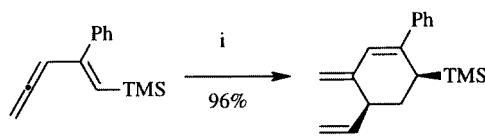
Scheme 76 Reagents and conditions: i, **29**, hexane; ii, NEt_3 , 3 M aq. NaOH , THF , 0°C ; iii, H_2O_2 .



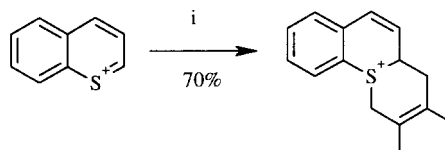
Scheme 77 Reagents and conditions: i, $\text{H}_2\text{C}=\text{CHCO}_2\text{Me}$, EtAlCl_2 , CH_2Cl_2 , 0°C .



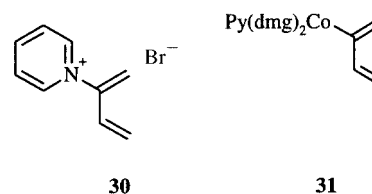
Scheme 78 Reagents and conditions: i, 2,3-dimethylbutadiene, CH_2Cl_2 , Δ .



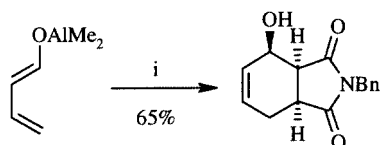
Scheme 79 Reagents: i, butadiene, $(\text{Ph}_3\text{P})_4\text{Pd}$ (cat.), THF .



Scheme 80 Reagents: i, 2,3-dimethylbutadiene, $\text{Cl}(\text{CH}_2)_2\text{Cl}$.



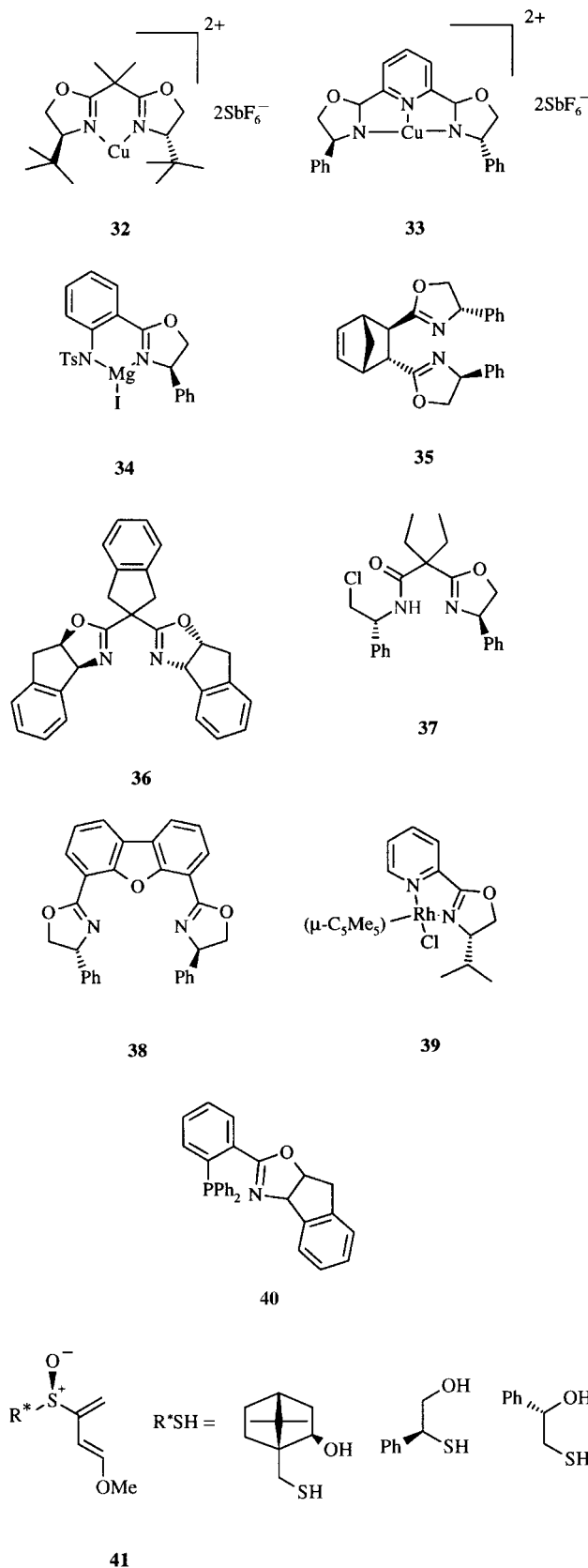
bulky aluminium based “designer” Lewis acids¹¹ have been recently described as powerful additives for the acceleration of Diels–Alder reactions. Aluminium dienolates undergo rapid, regio- and stereo-selective reactions with dienophiles (Scheme 81).²⁰³ Related “temporary covalent activation” of (*Z*)-2-chlorovinyltributylstannane by addition of catalytic amounts of dihaloboranes greatly accelerates its Diels–Alder reactions.²⁰⁴ Investigations of Lewis acid catalysis in water have been carried out. For example, use of 0.01 M copper(II) nitrate accelerates a reaction by 79 300 fold compared with the non-catalysed reaction in acetonitrile.²⁰⁵ Indium trichloride²⁰⁶ and methylrhenium trioxide²⁰⁷ are also effective catalysts in aqueous milieu. An investigation has been made into the cause of rate acceleration by lithium perchlorate in diethyl ether.²⁰⁸ Results suggest the effect cannot be due to internal pressure of the reagent system. The combination of lithium perchlorate in diethyl ether and high pressure is recommended as a useful tool for difficult cycloadditions.²⁰⁸ Other methods that have been used for rate enhancement include electrooxidation *in situ*,²⁰⁹ the use of novel solvents such as aqueous fluorinated alcohols,²¹⁰ supercritical water,²¹¹ supercritical carbon dioxide,²¹² microwave irradiation of reactions on a graphite support,²¹³ sonication²¹⁴ and initiation by radical cations.^{215,216}



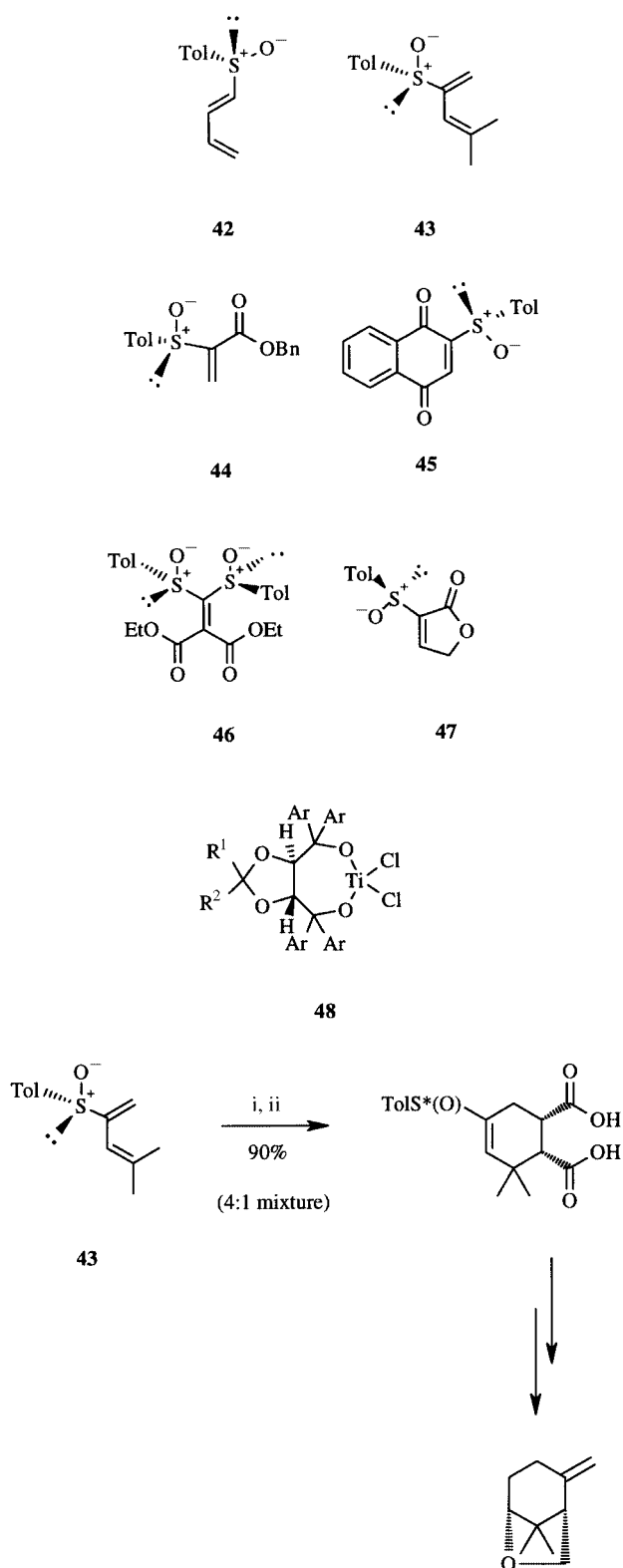
Scheme 81 Reagents and conditions: i, *N*-benzylmaleimide, THF–Et₂O, –70 °C.

5.3 Asymmetric intermolecular reactions

A large number of oxazoline and bis(oxazoline) metal complexes have been reported to allow effective asymmetric [4 + 2] cycloadditions. Among them are **32** (Evans),²¹⁷ **33** (Evans),²¹⁸ **34** (Fujisawa),²¹⁹ **35** (Takacs),²²⁰ **36** (I. W. Davies),²²¹ **37** (Yamauchi),²²² **38** (Kanemasa),²²³ **39** (D. L. Davies)^{224,225} and **40** (Catiavela).²²⁶ The effect of ligand bite angle²²⁷ and of solvent *versus* counterion effects²²⁸ on the enantioselectivity of [4 + 2] cycloadditions have also been studied. Another large block of work in the field of asymmetric Diels–Alder chemistry involves the reactions of homochiral sulfoxides of various kinds, either as the 4π or 2π component. Aversa²²⁹ has described the preparation and reactions of 3-alkylsulfinyl-1-methoxybuta-1,3-dienes such as **41**. Key observations were complete regioselectivity plus very high stereoselectivity on Lewis acid catalysed reactions with methyl acrylate and the control of diastereofacial selectivity by the chirality at sulfur. The related dienes **42**^{230,231} and **43**²³² have also been exploited, the latter in the synthesis of (–)-(1*S*,5*R*)-Karahana ether (Scheme 82). The synthesis and utility of the homochiral sulfinyl-1,3-dienes has been reviewed.¹⁰ On the other side of the coin, homochiral vinyl sulfoxides such as **44**,²³³ **45**,^{234,235} **46**²³⁶ and **47**²³⁷ have been used as dienophiles. In reactions of **45** with Dane’s diene, the regiochemistry of cycloaddition is reversed on the addition of a Lewis acid.²¹³ Sulfoxides **46** and **47** are quite unreactive, requiring high pressure to undergo cycloaddition with cyclopentadiene.^{236,237} Investigation of titanium TADDOLates as chiral catalysts has revealed an unexpected influence of the substituents in the 2-position (R¹, R² in **48**) of the dioxolane ring on the stereo-selectivity of [4 + 2] cycloadditions.²³⁸ Other chiral catalysts used successfully in conjunction with Lewis acids include (*S*)-VAPOL (**49**),²³⁹ a diol (**50**)²⁴⁰ derived from (–)-menthone (intriguingly with this reagent, reversal of enantiofacial selectivity was observed simply by switching the solvent from dichloromethane to THF), boron based Lewis acid (**51**)²⁴¹ and hydroxy sulfoxides derived from (*R*)- or (*S*)-methyl 1-naphthyl

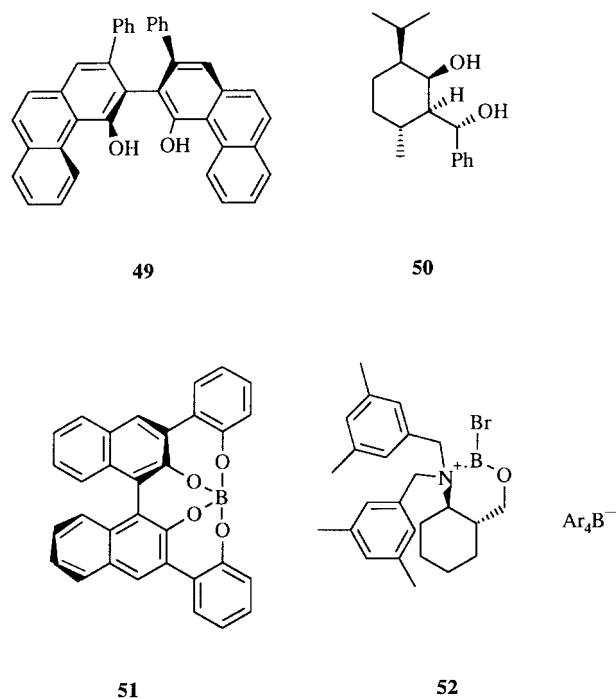


sulfoxide.²⁴² Corey has invoked a formyl hydrogen bond as a guide to the absolute stereochemistry of adducts formed in Diels–Alder reactions of aldehydes under chiral Lewis acid catalysis.^{243,244} The use of the cationic “super” Lewis acid **52** has allowed the first enantioselective reaction between cyclopentadiene and an acetylenic aldehyde to be observed.²⁴⁵ Supported reagents have become very popular, for example polymer-grafted titanium TADDOL complexes (poor ees),²⁴⁶ (–)-menthol–diethylaluminium chloride supported on silica or

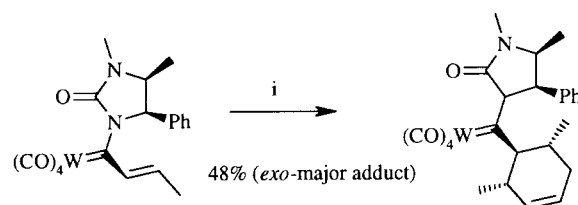


Scheme 82 Reagents and conditions: i, maleic anhydride, THF, Δ ; ii aq. Na_2CO_3 .

alumina (poor ees),²⁴⁷ polymer bound chiral amino alcohols—ethylaluminium dichloride (poor ees),²⁴⁸ titanium and zinc reagents supported on silica (poor *endo*:*exo* selectivity)²⁴⁹ and cross linked *N*-arylsulfonyl valine derivatives (good ees).²⁵⁰ The development of new chiral auxiliaries continues unabated. Boeckman has used homochiral camphor derived acrylamides in enantioselective approaches to (–)-cassioside²⁵¹ and a structural subunit of (+)-tetronolide.²⁵² Axially chiral auxiliary reagents used include 8,8'-BINOL (8,8'-dihydroxy-1,1'-binaphthalene)—here diastereoselectivities and *endo*:*exo* ratios



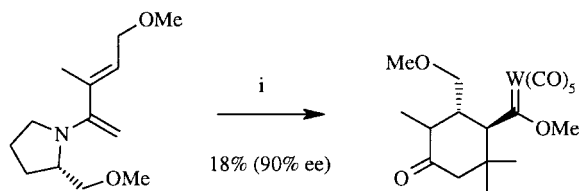
are highly dependent on the Lewis acid used²⁵³—and an *o*-*tert*-butyl *N*-acylanilide.²⁵⁴ Other new agents include *cis,cis*-spiro-[4,4]nonane-1,6-diol,²⁵⁵ monobenzylated isosorbide,²⁵⁶ new sultams derived from cyclopentadiene²⁵⁷ and diketopiperazines such as cyclo-(*S*)-phenylalanyl-(*R*)-proline.²⁵⁸ Electronic control of π -stacking in 8-phenylmethyl acrylates has been achieved using chromium carbonyl chemistry—the diastereomeric excess of the major *endo* adduct is clearly a function of the electron donor capacity of the complexed arene.²⁵⁹ It is difficult to deliberately perform asymmetric *exo*-selective Diels–Alder reactions, but using chiral tungsten carbene complexes Wulff has been successful (Scheme 83).²⁶⁰ In the opposite sense, Barluenga has reacted homochiral amino substituted dienes with tungsten carbene complexes to produce cyclohexanones in an enantioselective fashion (Scheme 84).²⁶¹ Homochiral aminobutadienes have allowed access to (–)- α -elemene *via* an asymmetric Diels–Alder reaction (Scheme 85).²⁶² The dioxaborolane **53** has been touted as a new enantioselective dienophile but enantiomeric excesses are very poor.²⁶³ A rather long winded enantioselective approach to a subunit of TaxolTM uses the already well-known furan **54** as the starting point.²⁶⁴ Langlois' asymmetric cationic Diels–Alder reaction of dioxolanylium species has often encountered difficulties in assignment of the diastereomeric excess—his group has recently advocated the use of deuterium NMR in chiral liquid crystals to reliably analyse the results.²⁶⁵ Homochiral orthoesters such as **55** on treatment with trimethylsilyl triflate or tin(IV) chloride give reactive cationic species that undergo asymmetric [4 + 2] cycloadditions with a variety of cyclic and acyclic dienes.²⁶⁶



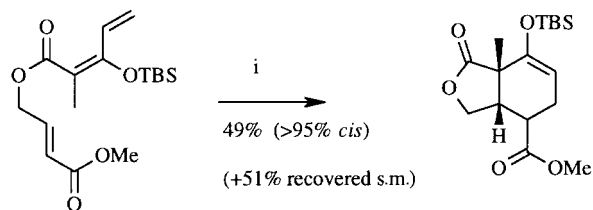
Scheme 83 Reagents and conditions: i, *trans*-piperylene, CH_2Cl_2 , Δ .

5.4 Intramolecular reactions

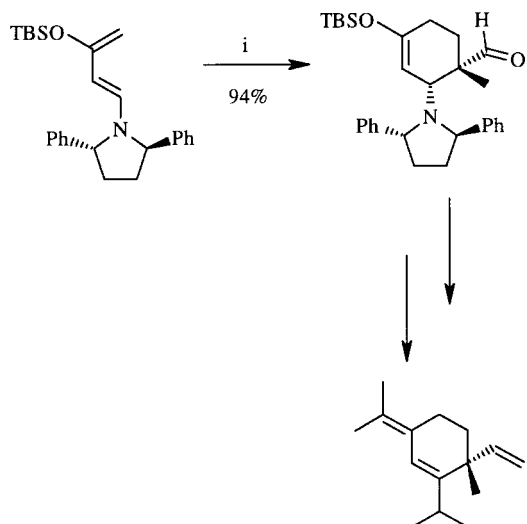
Page has recently introduced a brief intramolecular Diels–Alder (IMDA) approach to the core tricyclic structure of the daphnane and tigiane diterpenes (Scheme 86).^{267,268} The



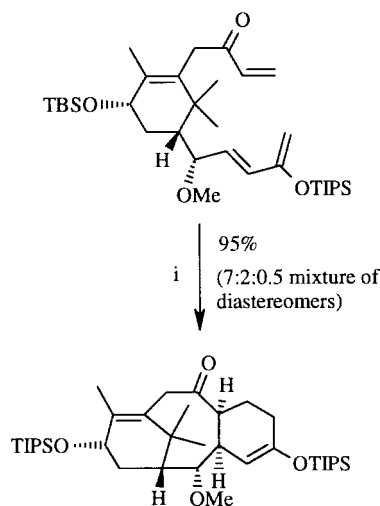
Scheme 84 Reagents: i, $\text{Me}_2\text{C}=\text{CHC}[\text{W}(\text{CO})_5]\text{OMe}$.



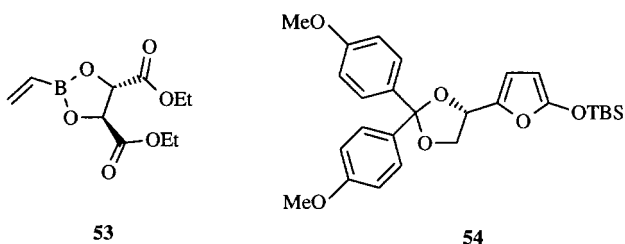
Scheme 87 Reagents and conditions: i, PhMe, Δ .



Scheme 85 Reagents: i, $\text{H}_2\text{C}=\text{C}(\text{Me})\text{CHO}$, PhMe.

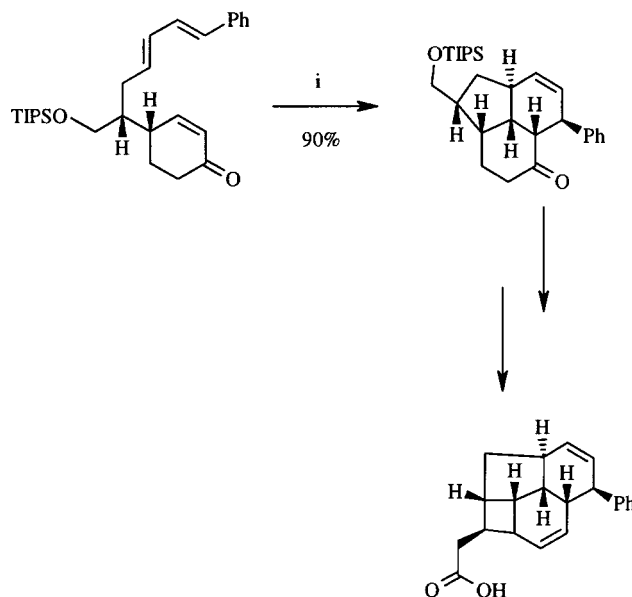


Scheme 88 Reagents and conditions: i, PhMe, 140°C , sealed tube.



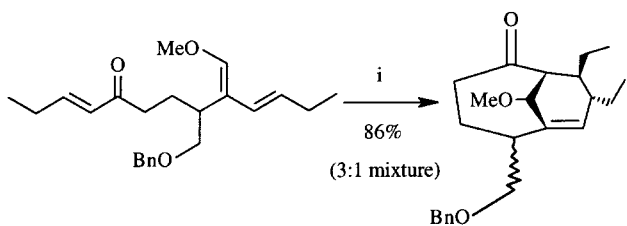
Scheme 86 Reagents and conditions: i, PhMe, Pr_3NEt_2 , 240°C , sealed tube.

diastereoselective synthesis of a potential Taxol™ C-ring precursor using the notoriously poor (for IMDA) ester linkage proceeded to give almost exclusively the undesired *cis*-fused product (Scheme 87).²⁶⁹ Somewhat more successful was Winkler's generation of the Taxol™ ABC ring system (Scheme 88).²⁷⁰ Grieco has provided an elegant synthesis of endiandric acid A using a deliberately conformationally restrained cyclohexenone that has to undergo cycloaddition *via* the *exo*-mode (Scheme 89).²⁷¹ The bicyclic core of the novel natural

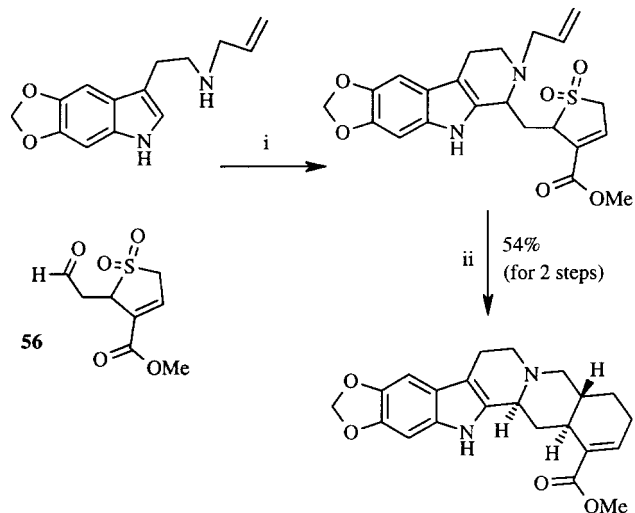


Scheme 89 Reagents: i, TFA (cat.), 5 M $\text{LiClO}_4\text{-Et}_2\text{O}$ or TMSOTf (cat.), CH_2Cl_2 .

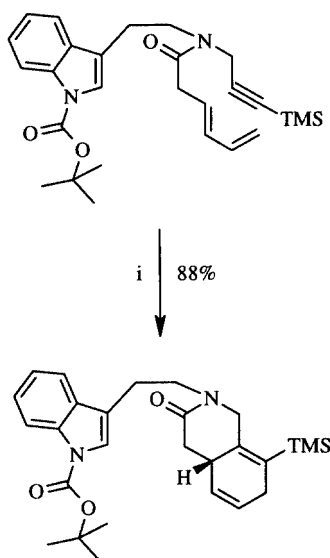
products CP-225,917 and CP-263,114 has been assembled *via* a dimethylaluminium chloride assisted reaction (Scheme 90).²⁷² An attractive one-pot tandem Pictet–Spengler–Diels–Alder sequence using 3-sulfolenes (**56**) provides a rapid assembly of the apoyohimbines (Scheme 91).²⁷³ An elegant transition metal-catalysed approach to such alkaloids has also been described (Scheme 92).²⁷⁴ Jacobi has continued to exploit the intramolecular Diels–Alder reactions of oxazoles, in this instance in a total synthesis of (\pm)-stemoamide (Scheme 93).²⁷⁵ The type two intramolecular Diels–Alder reaction, in which the dienophile is attached to the 2-position rather than the 1-position of the diene has been used by Shea in an approach to fused cycloheptanes and cyclooctanes (Scheme 94) and thence to



Scheme 90 Reagents and conditions: i, Me_2AlCl , CH_2Cl_2 , -10°C .

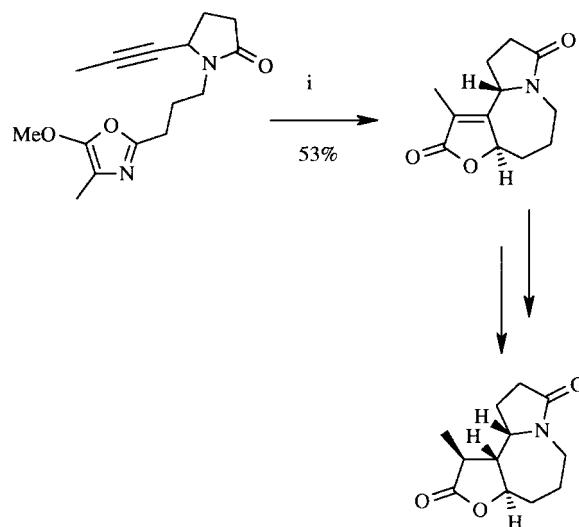


Scheme 91 Reagents and conditions: i, **56**, AcOH; ii, PhMe, Δ .

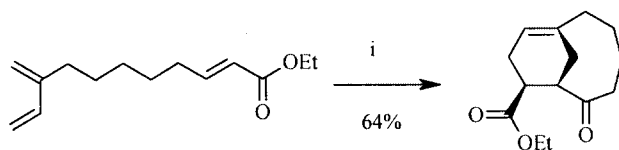


Scheme 92 Reagents: i, cat. $\text{Ni}(\text{COD})_2$, $\text{P}[\text{OCH}(\text{CF}_3)_2]_3$, THF.

total syntheses of ledol, ledene and compressanolide.²⁷⁶ The use of masked *o*-benzoquinones has led to a novel tandem Diels–Alder–Cope rearrangement procedure for the stereocontrolled synthesis of *cis*-decalins (Scheme 95).²⁷⁷ Similar chemistry has produced a route to (\pm)-xestoquinone.²⁷⁸ A new oxidative cycloaddition of *o*-[(ω -phenylthioethyl)acyl]phenols involving silylene protection produces the *peri*-hydroxy functionality present in some fused aromatic systems (Scheme 96).²⁷⁹ The trityl group has been used as a removable steric buttress to drive a furan Diels–Alder reaction virtually to completion. (Scheme 97).²⁸⁰ Other groups on nitrogen (H, benzyl, substituted benzyl) gave an equilibrium mixture of starting material and product, greatly favouring (>90%) the former. Vinyl sulfonamides successfully react in an intramolecular sense with furans (Scheme



Scheme 93 Reagents and conditions: i, diethylbenzene, Δ .

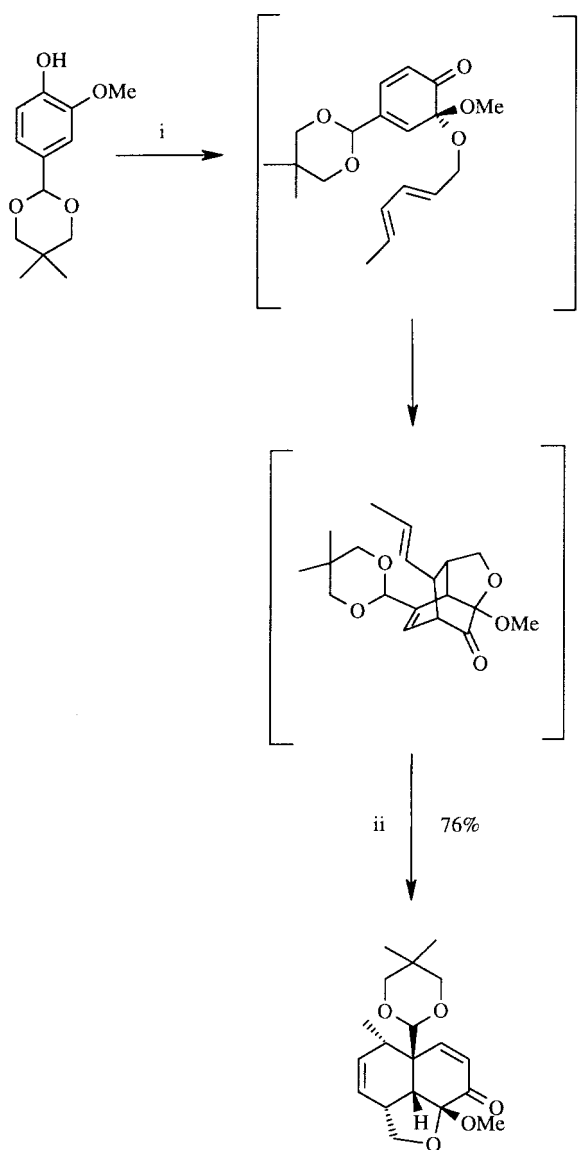


Scheme 94 Reagents and conditions: i, xylenes, 240°C , sealed tube.

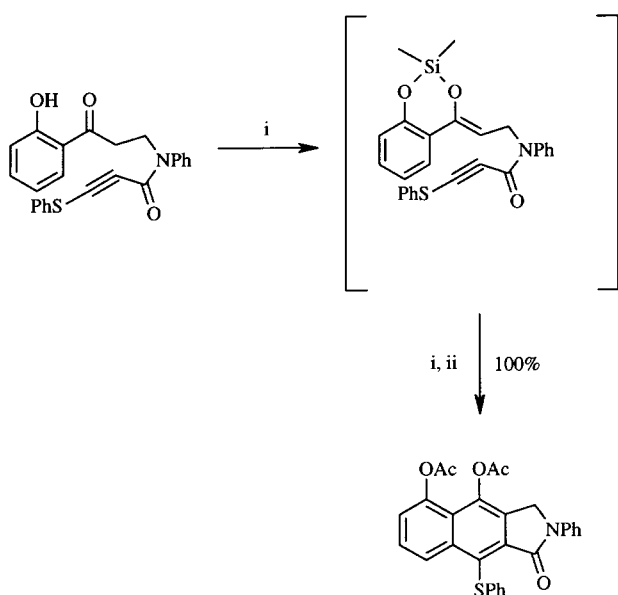
98).²⁸¹ Himbert has continued to demonstrate that allenecarboxamides²⁸² and allenyl esters²⁸³ undergo extraordinary (some occur at room temperature!) intramolecular Diels–Alder reactions with naphthalene acting as the diene (Scheme 99). The *in situ* hydroboration of alkynes to generate alkenylboranes, followed by intramolecular [4 + 2] cycloaddition and oxidation provides a route to functionalised bicyclo[4.3.0]nonenes and related tricyclic structures (Scheme 100).²⁸⁴

5.5 Asymmetric intramolecular reactions

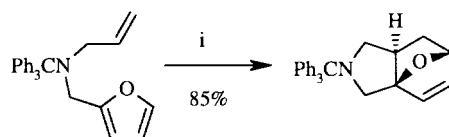
Evans has used both chiral bis(oxazoline) copper(II) catalysis²⁸⁵ and his well described *N*-acylimide chiral auxiliary chemistry²⁸⁶ in asymmetric routes to the natural products (–)-isopul’upone (Scheme 101) and α -himachalene (Scheme 102) respectively. Shing reports using (*S*)-(+)-carvone as a starting material for preparing the pentacyclic quassinoid skeleton in an enantioselective manner.²⁸⁷ In an IMDA approach to the natural products (+)-himbeline and (+)-himbacine, Hart initially observed problems with obtaining the desired *endo anti*-isomer from cycloaddition of trienes **57**. However, the use of the *thioester* and acid catalysis with silica–diethylaluminium chloride (Scheme 103) gave the desired isomer as the major product (*endo:exo* 20:1).²⁸⁸ The use of high pressure in the IMDA reaction of triene **58** allows access to a key precursor for the enantioselective synthesis of (+)-6-*epi*-mevinolin (Scheme 104).²⁸⁹ Starting from *L*-alanine methyl ester, oxazole chemistry has been used to prepare the alkaloid (–)-normalindine (Scheme 105).²⁹⁰ The use of remote allylic substituents on the diene has been shown to influence the stereochemical outcome of IMDA reactions of (*Z*)-olefins; high selectivity for the *exo*-adduct and high diastereofacial selectivity are observed (Scheme 106).²⁹¹ Preparation of enantiopure functionalised cyclohexen-2-ones from *D*-glucose and subsequent elaboration yields polyoxygenated decalins (Scheme 107).²⁹² Diels–Alder reactions of sugar derived trienoates can occur in a highly stereoselective manner. Thus the *L-arabino* derived triene **59** gives bicycle **60** as the sole product (Scheme 108).²⁹³ A synthetic route to the tricyclic drimane core of the mniopetals starts from *D*-mannitol (Scheme 109).²⁹⁴ Unusual polycyclic oxanorborn-



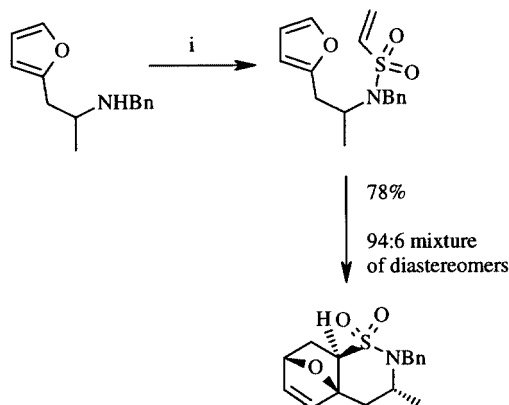
Scheme 95 Reagents and conditions: i, $(\text{CF}_3\text{CO}_2)_2\text{IPh}$, $\text{MeCH}=\text{CHCH}=\text{CHCH}_2\text{OH}$, THF; ii, mesitylene, Δ .



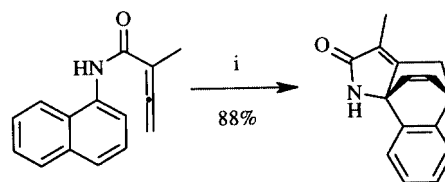
Scheme 96 Reagents and conditions: i, Me_2SiCl_2 , NEt_3 , chloranil, PhH, 100°C , sealed tube; ii, Ac_2O , pyridine.



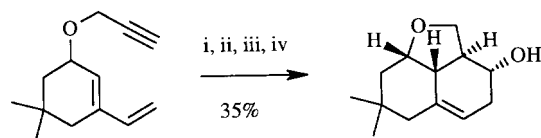
Scheme 97 Reagents and conditions: i, PhMe, Δ .



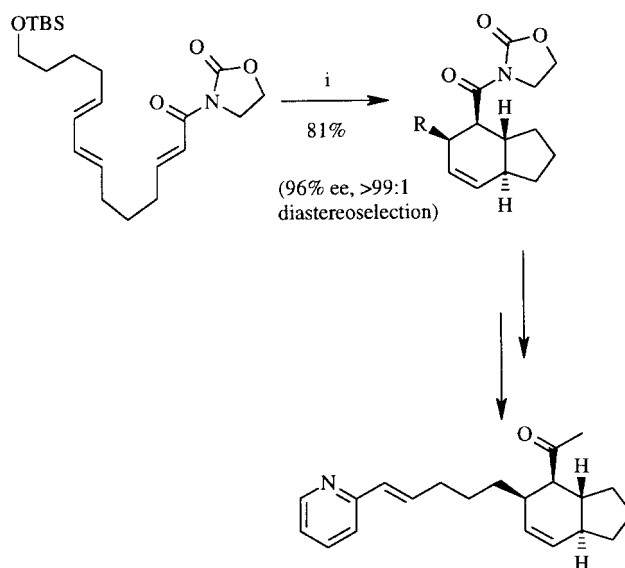
Scheme 98 Reagents: i, $\text{H}_2\text{C}=\text{CHSO}_2\text{Cl}$, NEt_3 , CH_2Cl_2 .



Scheme 99 Reagents and conditions: i, xylene, Δ .



Scheme 100 Reagents and conditions: i, $(\text{C}_6\text{H}_{11})_2\text{BH}$, THF; ii, BHT (butylated hydroxy toluene) (cat.), THF-PhH, Δ ; iii, Me_3NO , THF-PhH, Δ ; iv, H_2O , 60°C .

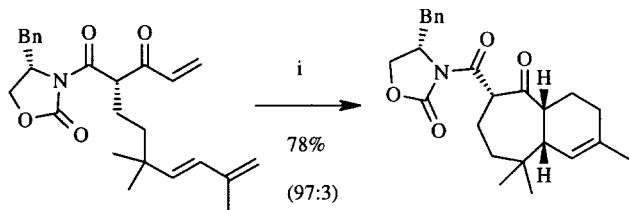


Scheme 101 Reagents: i, **32** (cat.), CH_2Cl_2 .

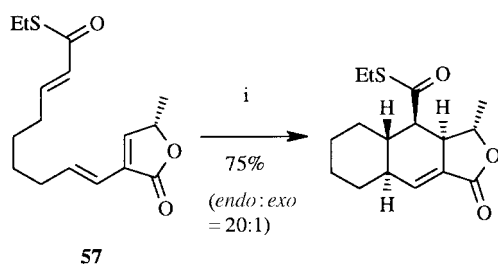
anes have been prepared from epoxyhexopyranosides by ring contraction followed by IMDA (Scheme 110).²⁹⁵

5.6 Transannular reactions

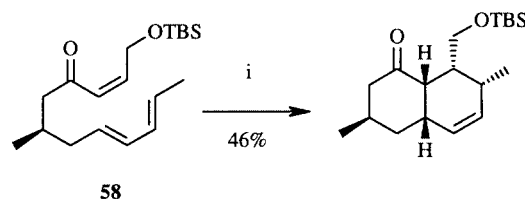
Deslongchamps, for long the pioneer of transannular cyclo-



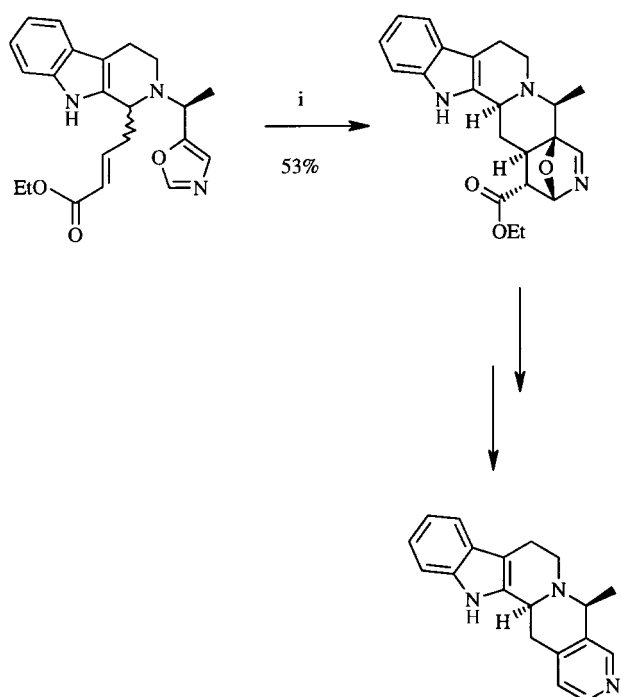
Scheme 102 Reagents and conditions: i, ZnBr₂, CH₂Cl₂, 0 °C.



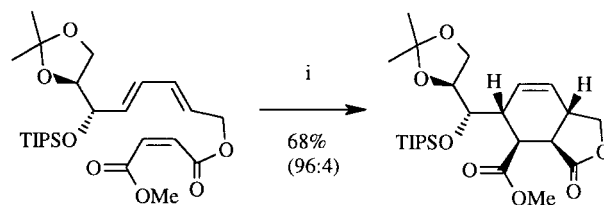
Scheme 103 Reagents and conditions: i, SiO₂-Et₂AlCl, PhMe, 40 °C.



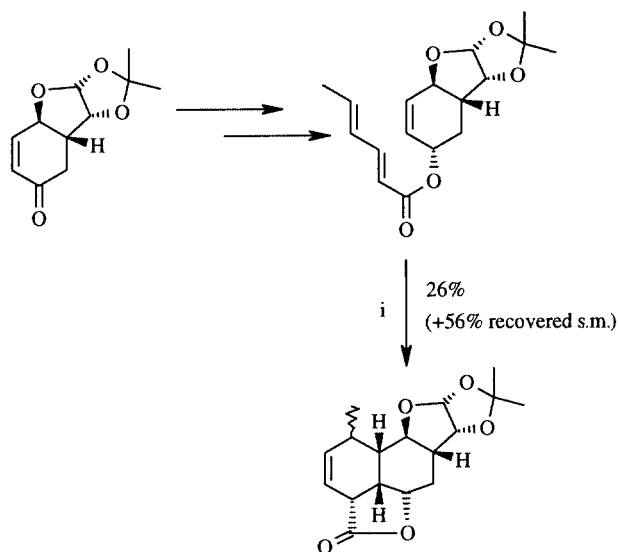
Scheme 104 Reagents and conditions: i, CH₂Cl₂, 10 kbar.



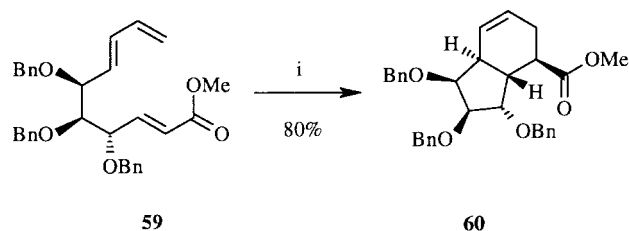
Scheme 105 Reagents and conditions: i, PhMe, Δ.



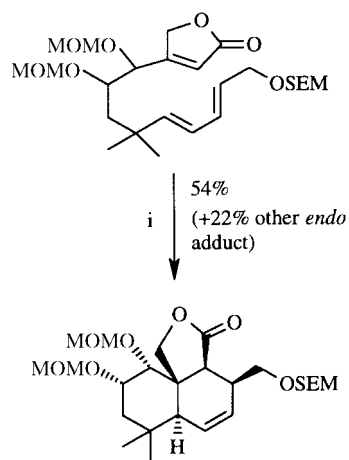
Scheme 106 Reagents and conditions: i, PhMe, Δ.



Scheme 107 Reagents and conditions: i, xylene, 200 °C, sealed tube.

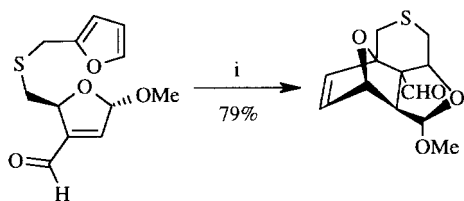


Scheme 108 Reagents: i, AlCl₃, PhMe-Et₂O.

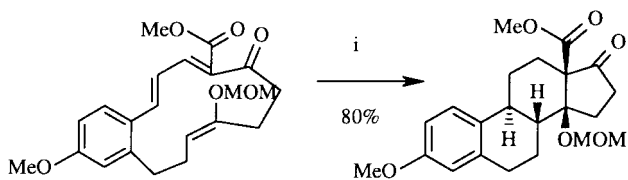


Scheme 109 Reagents and conditions: i, BHT (cat.), PhMe, 180 °C, sealed tube.

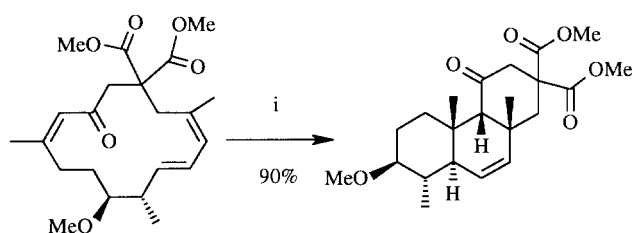
additions, has exploited the methodology in approaches to 5 α -steroids,²⁹⁶ 14 β -steroids (Scheme 111)²⁹⁷ and in an enantioselective route to building blocks for the quassinoids (Scheme 112).²⁹⁸ Starting from homochiral materials, Roush has initiated a transannular synthetic route to ikarugamycin²⁹⁹ but more impressively has assembled the complete carbon skeleton of nargenicin A₁ by a facile transannular cycloaddition of



Scheme 110 Reagents: i, SiO₂ chromatography.

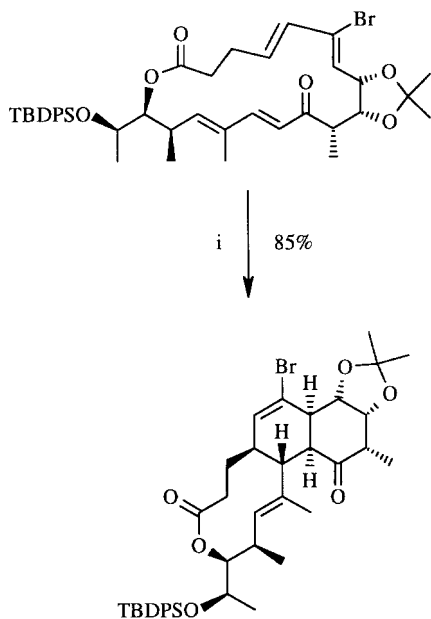


Scheme 111 Reagents and conditions: i, xylene, Δ.



Scheme 112 Reagents and conditions: i, PhMe, 220 °C, sealed tube.

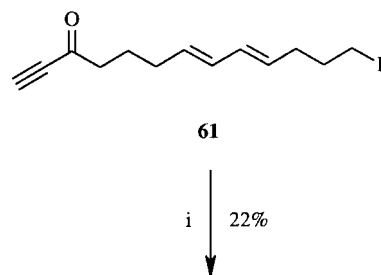
an 18-membered macrolide (Scheme 113).³⁰⁰ Radical-mediated equivalents are possible as elegantly demonstrated by Pattenden (Scheme 114).³⁰¹ Treatment of the iodonone **61** with tributyltin hydride and AIBN generates a radical that cyclises via the 13-*endo dig* mode. The resulting radical then undergoes a transannular cyclisation.



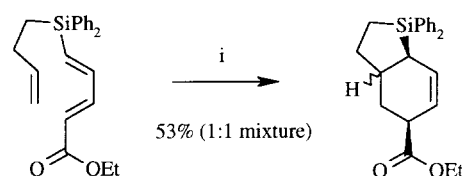
Scheme 113 Reagents and conditions: i, PhMe, 100 °C.

5.7 Tethered reactions

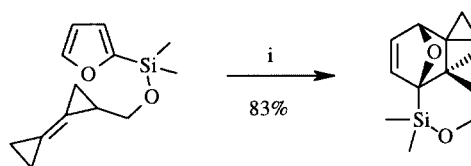
The use of temporary silicon tethers in intramolecular reactions has been reviewed by Sieburth.¹⁴ Other publications have concerned the preparation and utility of silyl substituted butadienes (Scheme 115)³⁰² and furans linked to bicyclopropylidene (Scheme 116).³⁰³ Craig³⁰⁴ and Fallis^{16,305} have investigated acetal tethers, the latter being particularly interested in tartrate derived isopropylidene acetals for enantio-



Scheme 114 Reagents and conditions: i, Bu₃SnH, AIBN, PhH, Δ.

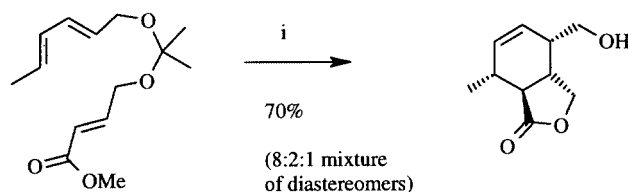


Scheme 115 Reagents and conditions: i, xylene, 180–200 °C, sealed tube.

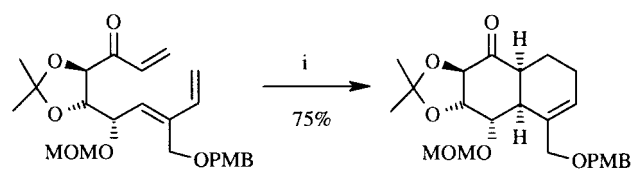


Scheme 116 Reagents and conditions: i, Et₂O, 130 °C, 10 kbar.

selective processes. Representative examples are shown (Schemes 117, 118). Fallis has also examined planar tether groups (double bonds and aromatic rings) and found facilitation of the cycloaddition.³⁰⁶ Tethering of 1-alkoxybutadienes to acrylate esters allows the formation of medium-sized lactones (Scheme 119).³⁰⁷ An enantioselective synthesis of the structurally unusual sesquiterpenoid (–)-myltaylenol involves the use of a sulfonate linker (Scheme 120).³⁰⁸



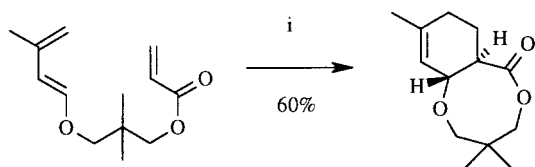
Scheme 117 Reagents and conditions: i, PhMe, 165 °C.



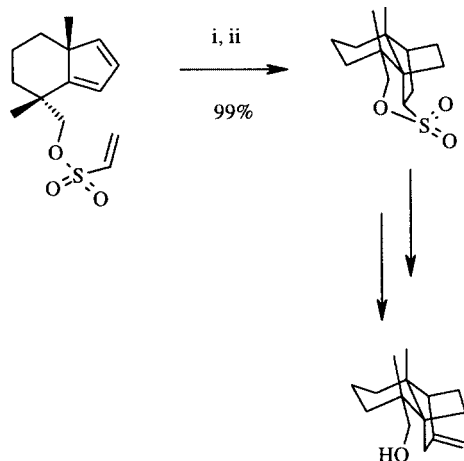
Scheme 118 Reagents and conditions: i, CH₂Cl₂, Δ.

5.8 Tandem reactions

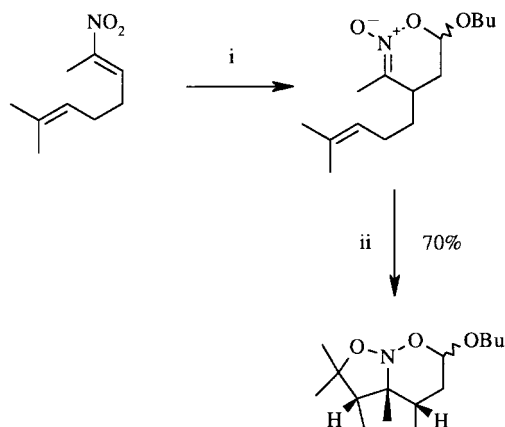
Denmark has once again published extensively on the tandem [4 + 2]/[3 + 2] cycloadditions of nitroalkenes. Examples bearing a two methylene tether (Scheme 121),³⁰⁹ approaches to (–)-rosmarinecine (Scheme 122),³¹⁰ (+)-crotanecine,³¹¹ (–)-



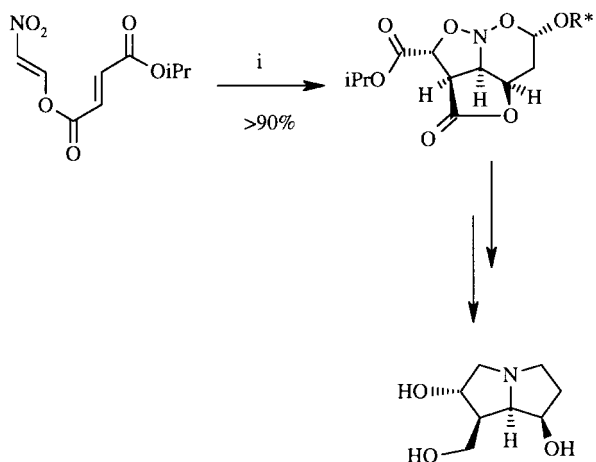
Scheme 119 Reagents and conditions: i, PhCN, Δ .



Scheme 120 Reagents: i, PhMe, Δ ; ii, Pd/C, H₂, THF.



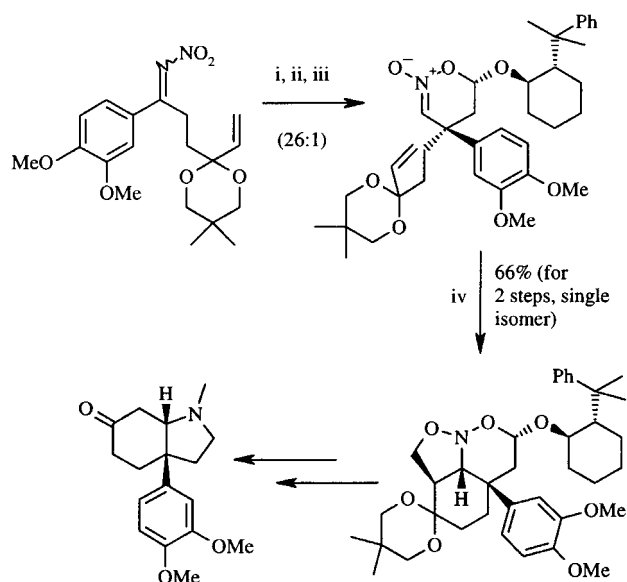
Scheme 121 Reagents and conditions: i, TiCl₂(OPr^t)₂, CH₂Cl₂, -78 °C; ii, NaHCO₃, PhH, Δ .



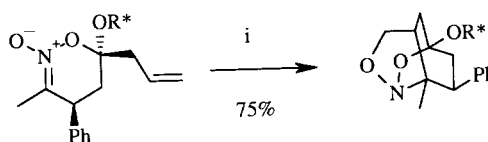
Scheme 122 Reagents and conditions: i, H₂C=CHOR*, methylaluminium bis(2,6-diphenylphenoxide) (MAnPh), CH₂Cl₂, -75 °C.

detoxinine,³¹² (-)-mesembrine (Scheme 123),³¹³ the use of *trans*-2-(1-methyl-1-phenylethyl)cyclohexanol as a new auxiliary,³¹⁴ the use of a new bridged mode of addition (Scheme 124),³¹⁵ and an asymmetric synthesis of highly functionalised

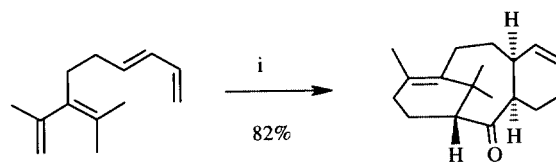
aminocyclopentanes.³¹⁶ Scheeren has demonstrated acceleration of tandem [4 + 2]/[3 + 2] cycloadditions of nitroalkenes by the use of high pressure.³¹⁷ Winkler has successfully used the tandem Diels–Alder reaction in an exceptionally brief (two steps) approach to the B/C *cis*-fused taxane nucleus (Scheme 125)³¹⁸ and in the synthesis of cyclopropyl taxane analogues.³¹⁹ Lautens has pioneered the use of the tandem “pincer” Diels–Alder reaction as an efficient method for the stereocontrolled synthesis of decalins³²⁰ and bridged polyheterocyclic systems (Scheme 126).³²¹ The Diels–Alder reaction has been used in tandem sequences with other powerful bond-forming reactions, for example the synthesis of pentacyclic steroids using a tandem Stille coupling–Diels–Alder route³²² and a domino Heck–Diels–Alder approach to bicyclo[4.3.0]nonenes.³²³



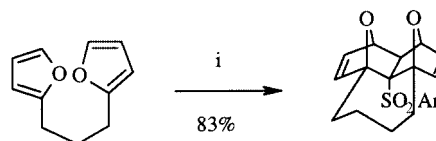
Scheme 123 Reagents and conditions: i, methylaluminium bis(2,6-di-*tert*-butyl)-4-methylphenoxide (MAD), PhMe, -10 °C; ii, H₂C=CHOR*, PhMe, -10 °C; iii, MAD, PhMe, -10 °C; iv, PhH, Δ .



Scheme 124 Reagents and conditions: i, K₂CO₃, PhMe, Δ .



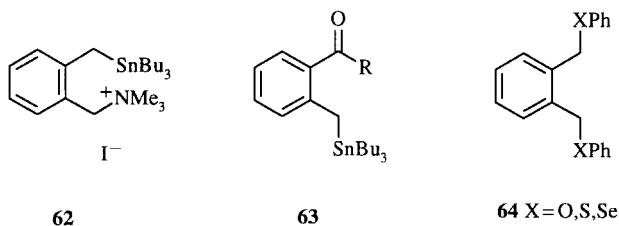
Scheme 125 Reagents and conditions: i, divinyl ketone, BF₃·OEt₂, PhMe, -70 °C.



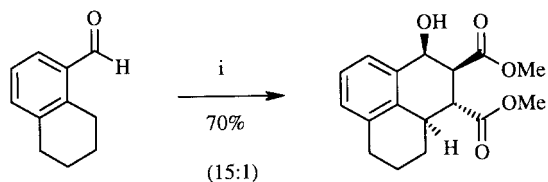
Scheme 126 Reagents: i, ArSO₂C≡CH, 5 M LiClO₄-Et₂O.

5.9 *o*-Quinodimethanes, *o*-quinone methides and related species

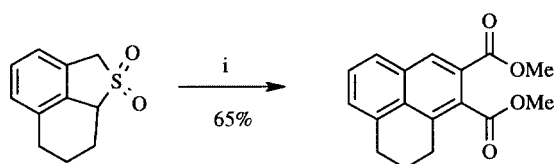
New methods for the generation of *o*-quinodimethanes include treatment of **62** with caesium fluoride,³²⁴ one-electron reduction of **63** using zinc,³²⁵ excimer laser photolysis of **64**,³²⁶ photo-



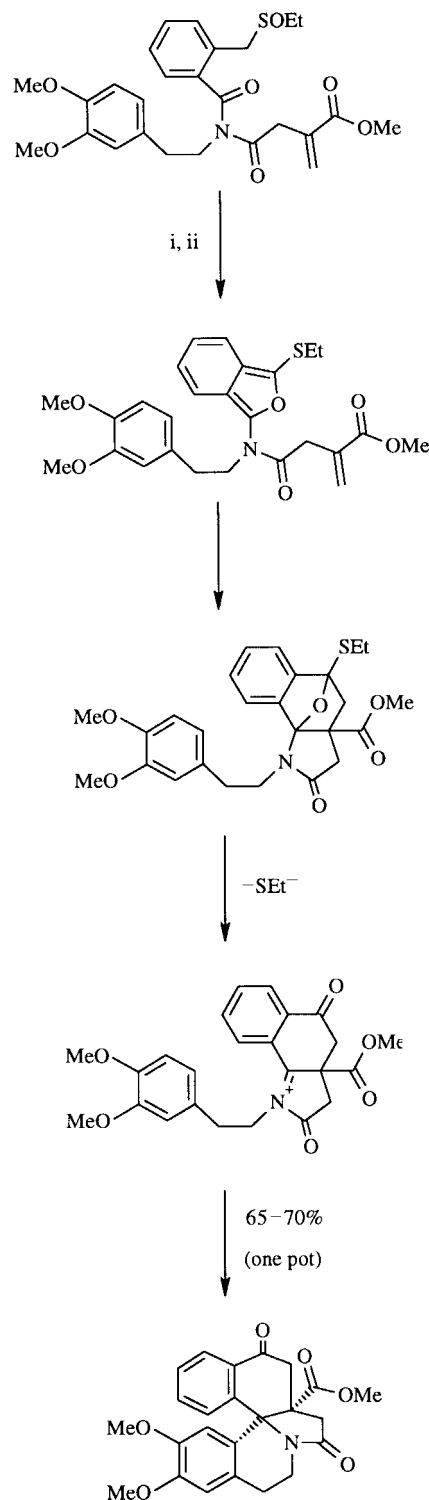
enolisation of bicyclic aldehydes and ketones (Scheme 127)³²⁷ and the use of tricyclic sulfones (Scheme 128).³²⁸ Thermolysis of a benzocyclobutene has been used in an IMDA approach to pisiferol.³²⁹ Gas phase cycloaddition reactions of radical cations of *o*-quinodimethanes have been studied.³³⁰ Padwa has investigated the use of isobenzofurans generated by a Pummerer reaction in the synthesis of a variety of ring systems^{331,332} and in a tandem Diels–Alder–*N*-acyliminium ion cyclisation approach to the erythrina alkaloids (Scheme 129).³³³ The novel *o*-quinonoid heterocycle benzo[*c*]tellurophene has been prepared for the first time and its trapping reactions with dienophiles investigated.³³⁴ Furan analogues of *o*-quinodimethane have been generated from **65** by treatment with acetyl or mesyl chloride in pyridine³³⁵ and also from the thermolysis of furan-fused 3-sulfolenes **66**.³³⁶ Thiophene and pyrrole analogues are prepared in a similar way from **67** and **68** respectively.^{337,338} Thiazole equivalents require treatment of **69** with *N*-bromosuccinimide.³³⁹ Pyridine *o*-quinodimethanes have been prepared from **70** and **71** by treatment with sodium iodide.³⁴⁰ Thermolysis of **72** yields a pyrimidine *o*-quinodimethane.³⁴¹ Benzofuran analogues result from **73** by reaction with TBAF.³⁴² Benzofuran, benzothiophene and indole analogues can also be generated from the sulfolenes **74**.³⁴³ Alternative approaches to indole *o*-quinodimethane equivalents involve **75**, **76** and **77**.^{344–346} Sulfolenes **78** and **79** can be used to prepare carbazole and quinolone *o*-quinodimethanes respectively.^{347,348} The sultine **80** serves as a precursor to a quinoxaline *o*-quinodimethane.³⁴⁹ Photolysis^{350,351} allows *in situ* generation of an *o*-quinone methide that undergoes an IMDA reaction.³⁵⁰ An alternative procedure for their generation is by oxidation with DDQ; this has been used in a synthesis of euglobal-G3 and euglobal-G4.³⁵² Nair has reviewed recent developments in the cycloadditions of *o*-benzoquinones.²⁹ The use of *o*-hydroxythiophthalimides such as **81** allows access to *o*-thioquinones.^{353,354} A retro-Diels–Alder reaction allows the generation and trapping of an *o*-thioquinone *S*-oxide (Scheme 130).³⁵⁵ A variety of methods exist for the generation of *o*-quinone methide imines, including thermal extrusion of carbon dioxide (Scheme 131)³⁵⁶ or sulfur dioxide (Scheme 132)³⁵⁷ and by Lewis acid treatment of appropriately substituted benzylic alcohols (Scheme 133).^{358,359}



Scheme 127 Reagents and conditions: i, MeO₂CCH=CHCO₂Me, MeCN, *hv*.



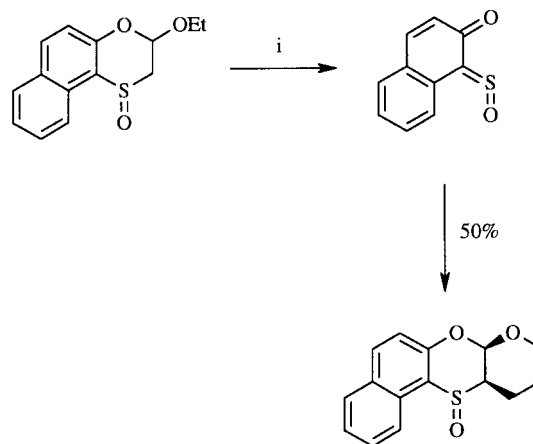
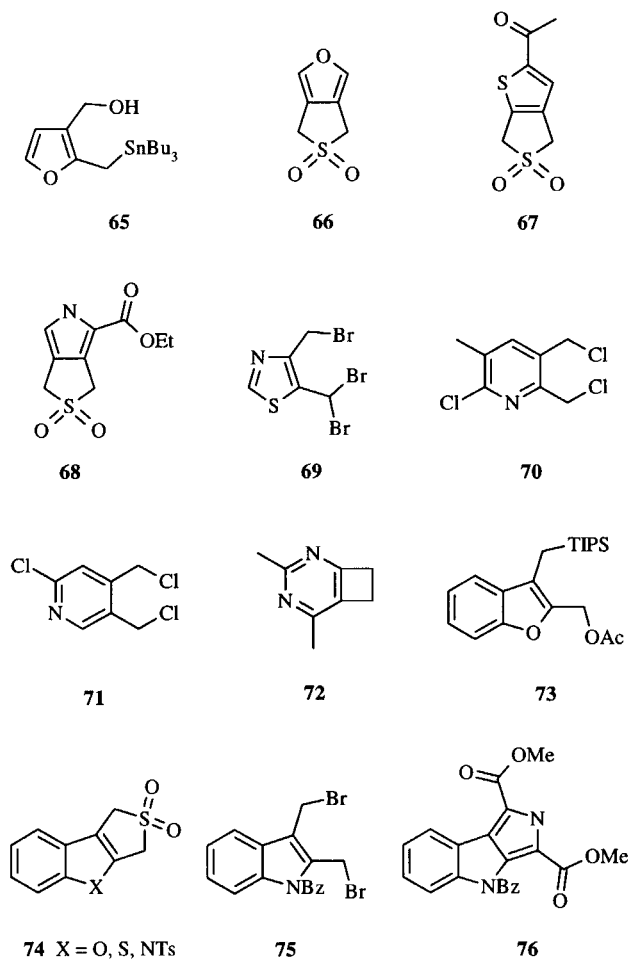
Scheme 128 Reagents and conditions: i, DMAD, 250–280 °C.



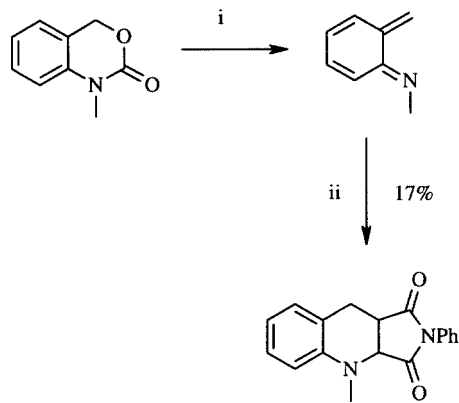
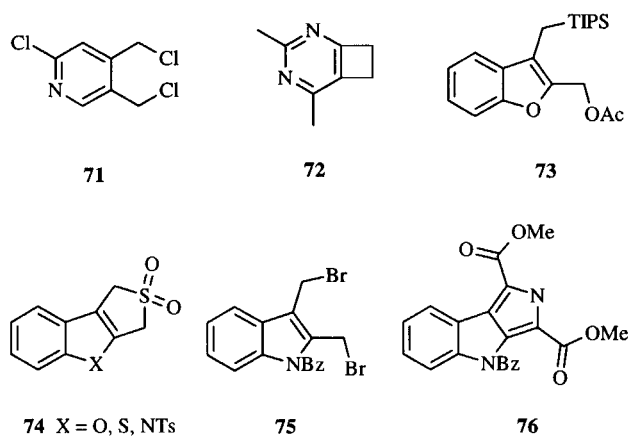
Scheme 129 Reagents and conditions: i, Ac₂O, *p*-TSA, PhMe, Δ; ii, *p*-TSA, PhMe, Δ.

5.10 Hetero Diels–Alder reactions

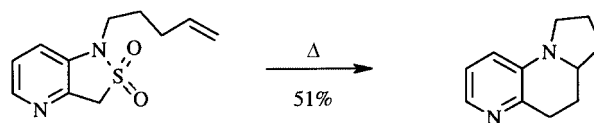
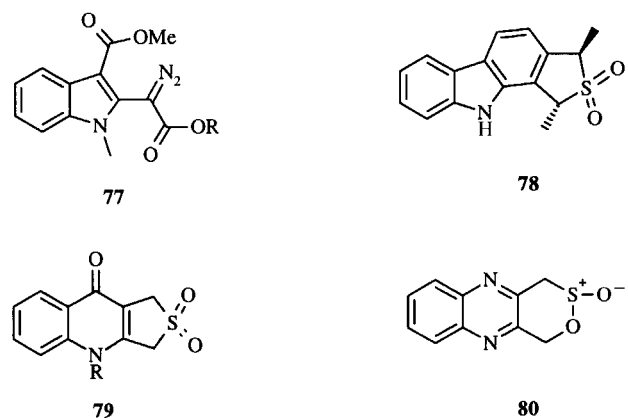
The reaction of 1-acetyl-2-benzylidene-2,3-dihydroindol-3-ones and 1,2-dihydro-3*H*-pyrrolo[2,3-*b*]pyridin-3-ones with enol ethers provides, after subsequent elaboration, a route to pyrano[2,3-*b*]indoles and 6-aza- δ -carboline respectively.^{360,361} Tricarbonyl(formyltrimethylenemethane)iron undergoes hetero-Diels–Alder reactions with dienes to yield deoxypyranosides tagged with the iron tricarbonyl manifold (Scheme 134).³⁶² A study has been made of the effect of ligand structure and acidity for a range of lanthanide catalysts used for the hetero-Diels–Alder reaction between crotonaldehyde and ethyl vinyl ether.³⁶³ Similarly, a study of the effect of



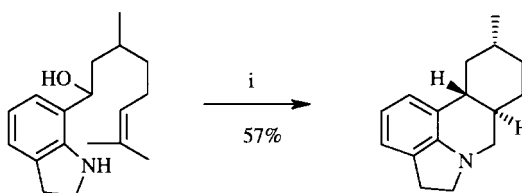
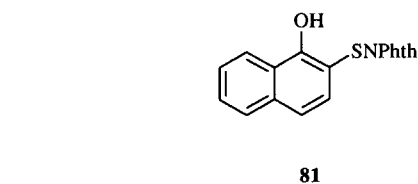
Scheme 130 Reagents and conditions: i, dihydropyran, CHCl_3 , Δ .



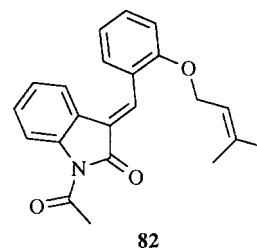
Scheme 131 Reagents and conditions: i, 1,2,4-trichlorobenzene, Δ ; ii, NPM.



Scheme 132

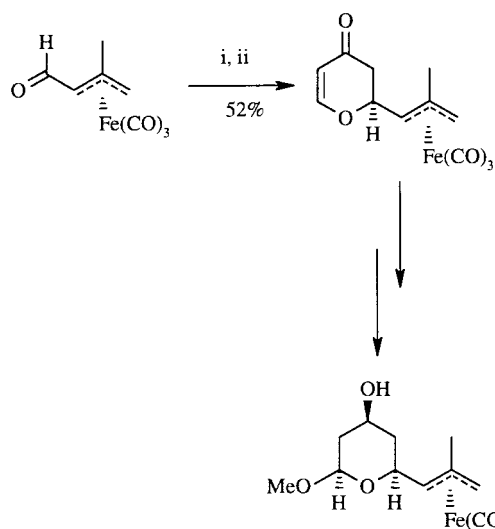


Scheme 133 Reagents: i, $\text{BF}_3 \cdot \text{OEt}_2$, $\text{Cl}(\text{CH}_2)_2\text{Cl}$.

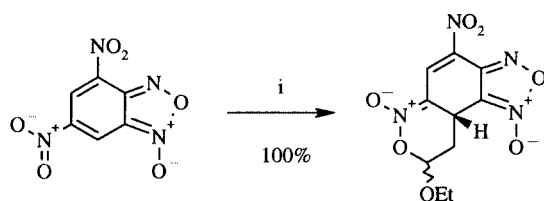


magnesium perchlorate on the competition between an intramolecular hetero-Diels–Alder and intramolecular ene reaction of **82** has been published.³⁶⁴ Trifluoromethanesulfonic acid,³⁶⁵ cationic palladium(II) complexes³⁶⁶ and polyclonal antibodies³⁶⁷ have all been reported to serve as novel catalysts for the hetero-Diels–Alder reaction. The nitro groups of 4,6-dinitrobenzofuroxan can participate in hetero-Diels–Alder reactions (Scheme 135).³⁶⁸ Cycloaddition of a number of species can lead to 1,2-oxazines and 1,4-oxazines. Thus vinyl nitroso compounds (Scheme 136),³⁶⁹ benzyloxy nitroso carb-

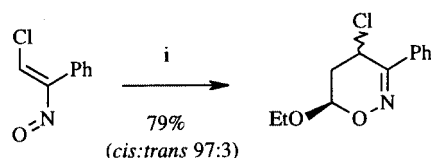
amate (Scheme 137)³⁷⁰ and aryl nitroso compounds (Scheme 138)³⁷¹ lead to 1,2-oxazines, the latter transformation being aided by the molybdenum catalyst **83**. On the other hand, *C*-arylimines lead to 1,4-oxazines.³⁷² Interestingly, 1,2-oxazines can serve as functional equivalents of 2-cyano-1-azadienes in IMDA reactions (Scheme 139).³⁷³ These dienes can also be pre-



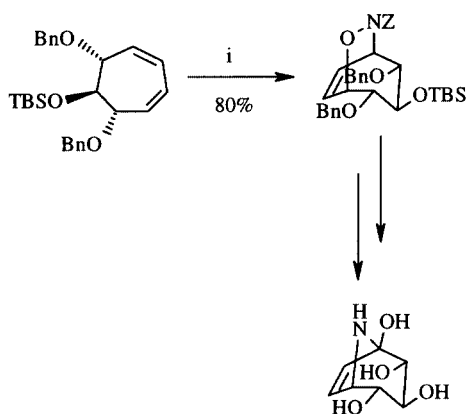
Scheme 134 Reagents: i, $\text{MeOCH}=\text{CHC}(\text{OTMS})=\text{CH}_2$, $\text{BF}_3 \cdot \text{OEt}_2$, Et_2O ; ii, TFA, CCl_4 .



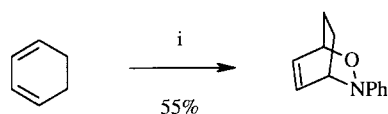
Scheme 135 Reagents: i, $\text{H}_2\text{C}=\text{CHOEt}$, CD_2Cl_2 .



Scheme 136 Reagents: i, $\text{H}_2\text{C}=\text{CHOEt}$.

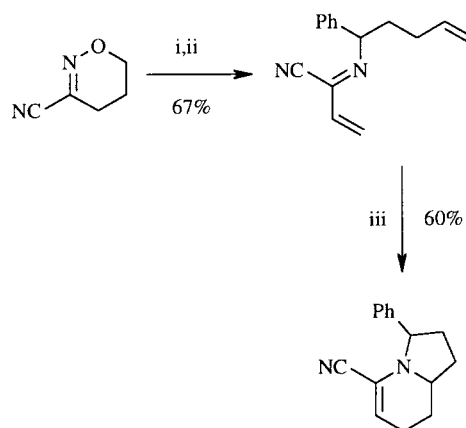
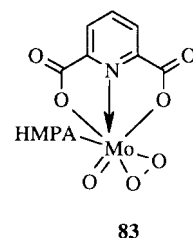


Scheme 137 Reagents and conditions: i, ZnHOH , Bu_4NIO_4 , CH_2Cl_2 , 0°C .

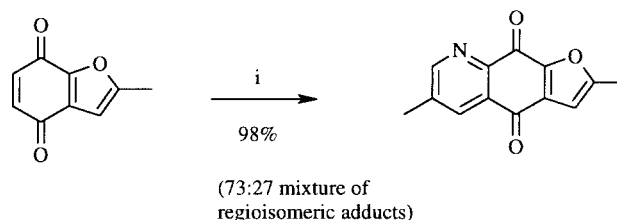


Scheme 138 Reagents: i, PhNH_2 , H_2O_2 , **83**.

pared from non-oxazine precursors.³⁷⁴ Activation of 1-azadienes can be accomplished by using an *N,N*-dimethylamino^{375–378} or a *tert*-butyldimethylsilyloxy³⁷⁹ substituent on the nitrogen. An example is shown in Scheme 140.³⁷⁷ Barluenga

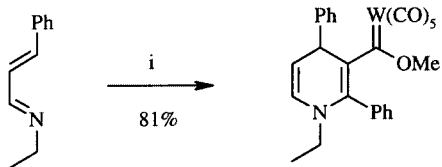


Scheme 139 Reagents and conditions: i, $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_2\text{CH}(\text{Br})\text{Ph}$, AgBF_4 , CH_2Cl_2 ; ii, NEt_3 , -60°C ; iii, FVP.

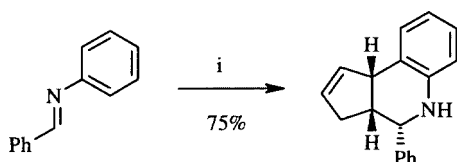


Scheme 140 Reagents: i, $\text{Me}_2\text{NN}=\text{CHC}(\text{Me})=\text{CH}_2$, EtOH .

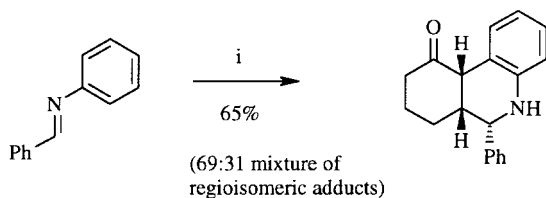
has demonstrated the first cycloaddition of both 1-azadienes³⁸⁰ and 2-azadienes³⁸¹ with Fischer carbene complexes (Scheme 141). Anhydrous indium trichloride has been found to catalyze the reaction of 2-azadienes with both cyclopentadiene and cyclohexenone (Schemes 142, 143).³⁸² Fortunak has used intramolecular hetero-Diels–Alder reactions of 2-azadienes as an approach to the topoisomerase inhibitor camptothecin.^{383,384} A number of imines, for example ethyl (*N*-tosylimino)acetate,³⁸⁵ methyl 2-aryl-2*H*-azirine-3-carboxylates³⁸⁶ and polymer-bound Schiff's bases³⁸⁷ have been found to act as the 2π -component in hetero-Diels–Alder reactions. Pyrazines bearing a tethered olefin undergo IMDA reactions to yield bicyclic structures (Scheme 144).³⁸⁸ Reactions of 4,5-dicyanopyridazines with olefins provides a route to novel caged structures that are formed from the primary cycloadduct by extrusion of nitrogen.^{389,390} Intramolecular hetero-Diels–Alder reactions of 1,2,4-triazines with imidazole acting as the dienophile (Scheme 145)³⁹¹ and of 1,2,4,5-tetrazines with indole serving as the dienophile (Scheme 146)³⁹² have both been reported by Snyder. The synthesis of pyridazines substituted by silyl, germyl or stannyl moieties can be achieved by cycloaddition of 1,2,4,5-tetrazine with the appropriate metallated alkyne.³⁹³ The cycloaddition chemistry of 3-methoxy-6-methylthio-1,2,4,5-tetrazine has been described.³⁹⁴ Thermolysis of various sulfoxides leads to thioaldehyde intermediates that can be trapped with dienes (Scheme 147).³⁹⁵ Thiobenzophenones react with benzyne (Scheme 148)³⁹⁶ and other dienophiles³⁹⁷ to provide cycloadducts. The related *p*-thioquinone methides can also be trapped with butadienes to give spiro cycloadducts.³⁹⁸ Thio-



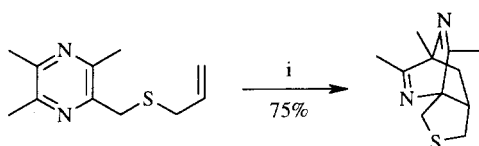
Scheme 141 Reagents: i, $\text{PhC}\equiv\text{CC}[\text{W}(\text{CO})_5]\text{OMe}$, THF.



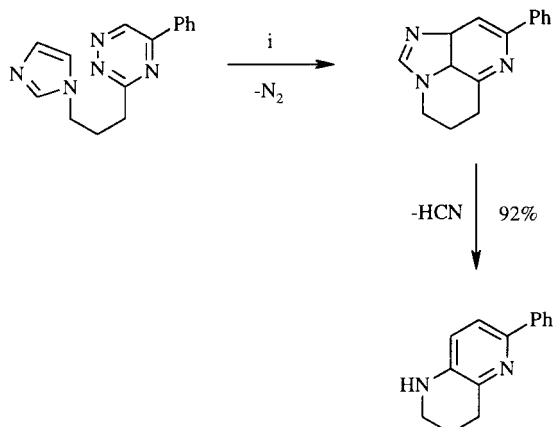
Scheme 142 Reagents: i, cyclopentadiene, InCl_3 , MeCN.



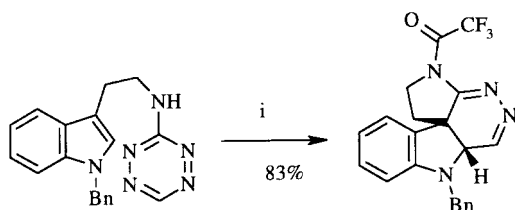
Scheme 143 Reagents: i, cyclohexenone, InCl_3 , MeCN.



Scheme 144 Reagents and conditions: i, TFA, Δ .

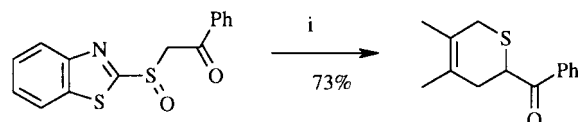


Scheme 145 Reagents and conditions: i, 1,3,5-tri-isopropylbenzene, BHT, Δ .

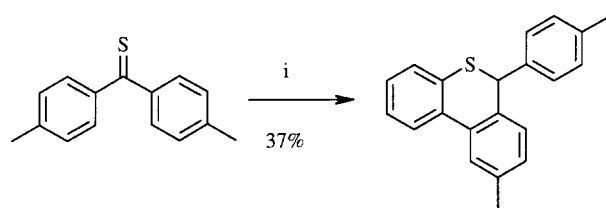


Scheme 146 Reagents and conditions: i, TFAA, dioxane, Δ .

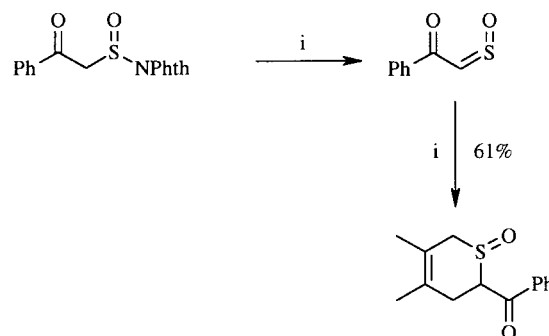
aldehyde *S*-oxides can be generated under mild conditions and then undergo cycloadditions with dienes (Scheme 149).³⁹⁹ Thiopyrans can also be prepared by hetero-Diels–Alder reactions of *N*-acylthioformamides (Scheme 150)⁴⁰⁰ and from reactions of 4-*N,N*-dimethylamino-2-phenyl-1-thiobuta-1,3-diene (Scheme 151).⁴⁰¹ Oxathiins prepared from cycloadditions of



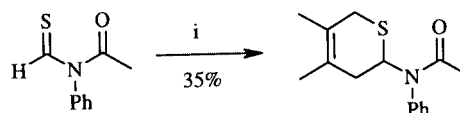
Scheme 147 Reagents and conditions: i, 2,3-dimethylbutadiene, dioxane, Δ .



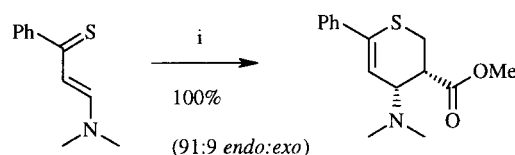
Scheme 148 Reagents and conditions: i, 'benzyne', PhMe, Δ .



Scheme 149 Reagents: i, pyridine, 2,3-dimethylbutadiene, CHCl_3 .



Scheme 150 Reagents: i, 2,3-dimethylbutadiene, TiCl_4 , CH_2Cl_2 .

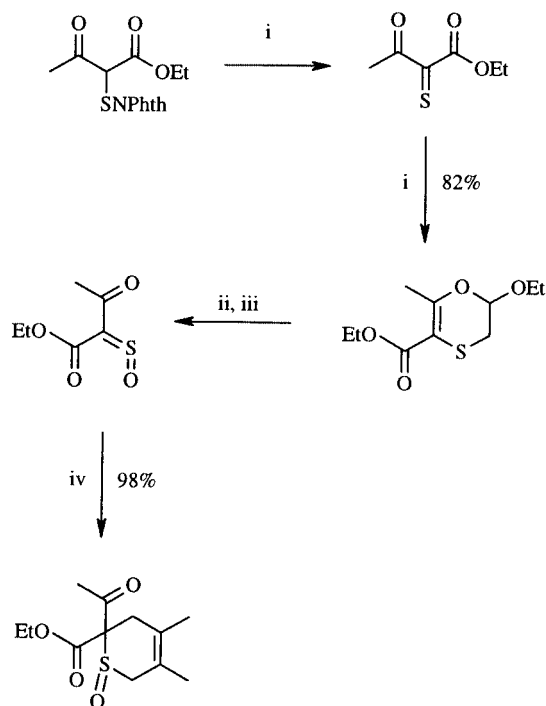


Scheme 151 Reagents and conditions: i, $\text{H}_2\text{C}=\text{CHCO}_2\text{Me}$, CH_2Cl_2 , -30°C .

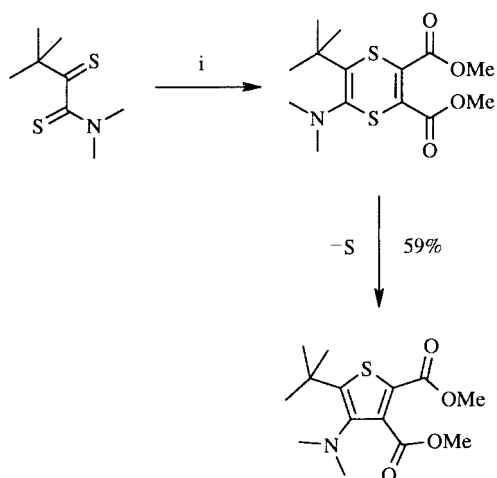
α,α' -dioxothiones undergo retro-Diels–Alder reactions generating α -oxosulfines that can subsequently be trapped by dienes (Scheme 152).⁴⁰² Thioxothioamides react with alkynyl esters (Scheme 153)⁴⁰³ and with isocyanates⁴⁰⁴ to give thiophenes after loss of sulfur from the primary cycloadduct.

5.11 Asymmetric hetero Diels–Alder reactions

Examples of homochiral oxadienes used in asymmetric hetero-Diels–Alder reactions include **84**, a benzylidene pyruvic acid attached to a derivative of *D*-(-)-erythronolactone [used in a synthesis of the lignan (-)-*O*-dimethylsugiresinol],^{405,406} the isoborneol sulfanyl diene **85** (used in lithium perchlorate catalysed synthesis of pyranoids)⁴⁰⁷ and Dondoni's galactopyranoside derived 3-(thiazol-2-yl)propenyltetrahydropyran **86**.⁴⁰⁸ Homochiral oxygenated 2π -components include Stoodley's salicylaldehyde **87**, a study of which has been made in Lewis acid catalysed additions to Danishefsky's diene,⁴⁰⁹ and the perennial (*S*)-(-)-2,3-*O*-isopropylidene glyceraldehyde **88**, used in a formal total synthesis of (+)-laurecin.⁴¹⁰ Popular catalysts for asymmetric cycloadditions of oxadienes are metal complexes of bis-oxazolines such as **89** (used with magnesium

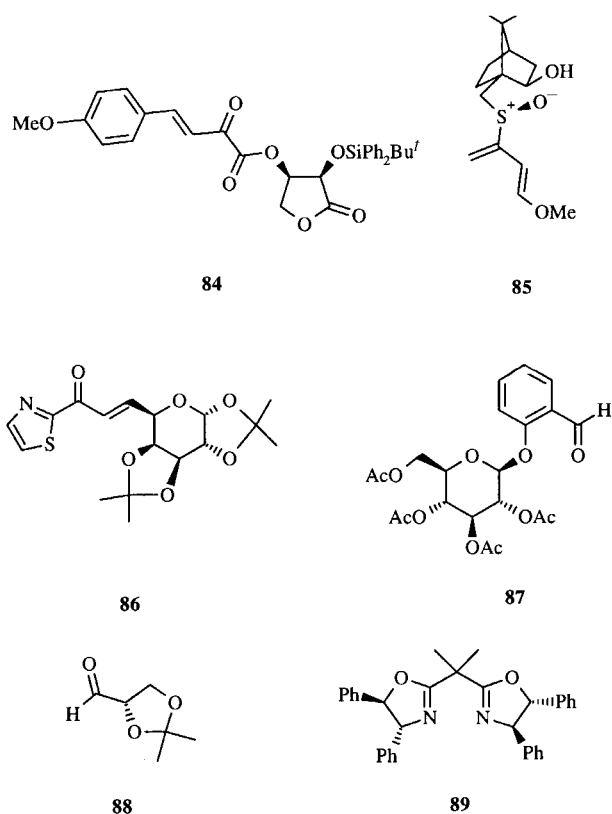


Scheme 152 Reagents and conditions: i, pyridine, $\text{H}_2\text{C}=\text{CHOEt}$, CHCl_3 ; ii, *m*-CPBA, CH_2Cl_2 , $-18\text{ }^\circ\text{C}$; iii, CHCl_3 , Δ ; iv, 2,3-dimethylbutadiene, CHCl_3 , Δ .

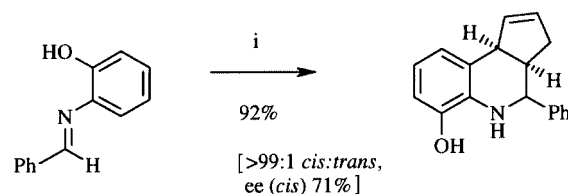


Scheme 153 Reagents: i, DMAD, CH_2Cl_2 .

perchlorate),⁴¹¹ **90** and **32** [used with copper(II) triflate],^{412–414} **91** [used with zinc(II) triflate]⁴¹⁵ and a homochiral ytterbium(III) phosphate complex.⁴¹⁶ Homochiral 2-alkenyloxazolines have been used in an approach to novel pyrimidones (Scheme 154).⁴¹⁷ A homochiral Lewis acid derived from ytterbium(III) triflate and (*R*)-(+)-BINOL has been used by Kobayashi in an enantioselective route to tetrahydroquinolines (Scheme 155).⁴¹⁸ Enantiomerically pure (*2R*)-4-oxopiperidone can be prepared from the homochiral imine **92**.⁴¹⁹ In related chemistry, the imine **93** also provides access to homochiral piperidones.⁴²⁰ Three component asymmetric aqueous hetero-Diels–Alder reactions involving homochiral isopropylidene glyceraldehydes, an amine salt and a diene have been reported.⁴²¹ The *N*-tosylimine **94** derived from (*2R*)-bornane-10,2-sultam undergoes Lewis acid catalysed asymmetric cycloadditions with cyclopentadiene.⁴²² Harwood has demonstrated the utility of (*5S*)-5-phenyl-5,6-dihydro-2*H*-1,4-oxazin-2-one **95** in hetero-Diels–Alder reactions.⁴²³ Homochiral iron tricarbonyl imines such as **96** react with Danishefsky's diene to provide an asymmetric route to the piperidine alkaloid SS20846A.⁴²⁴ Barluenga has used the diene **97** derived from (*S*)-2-methoxymethylpyrrolidine

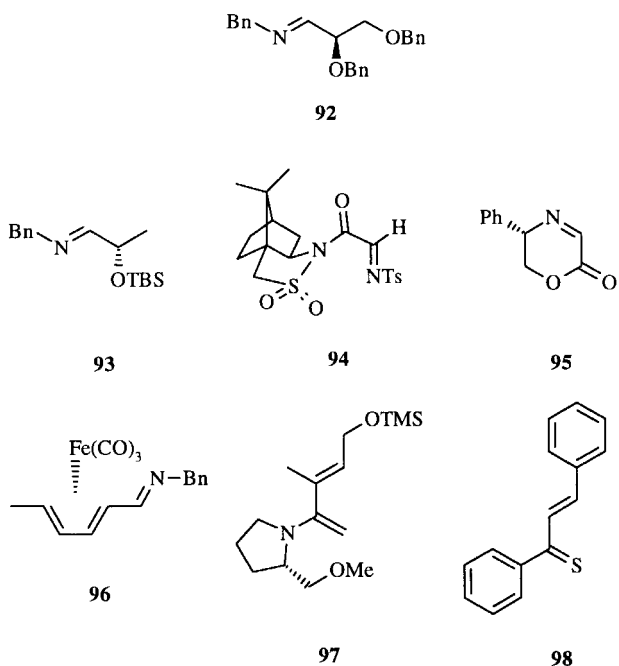


Scheme 154 Reagents and conditions: i, PhNCO , $150\text{ }^\circ\text{C}$, sealed tube.



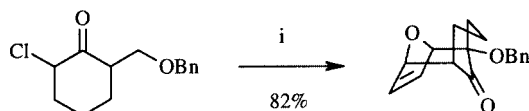
Scheme 155 Reagents: i, cyclopentadiene, $\text{Yb}(\text{OR}^*)_3$, 2,6-di-*tert*-butylpyridine, CH_2Cl_2 .

in syntheses of highly functionalised 4-piperidones.⁴²⁵ Saito has extensively investigated the asymmetric hetero-Diels–Alder reactions of thiochalcones (*e.g.* **98**) by examining thermal and Lewis acid catalysed reactions with di(-)-menthyl fumarate,⁴²⁶ with (*S*)-*N*-acryloyl-4-benzyl-1,3-oxazolidin-2-one under ytterbium(III) triflate,⁴²⁷ dimethylaluminium chloride⁴²⁸ or titanium(IV) chloride⁴²⁸ catalysis and with *N*-acryloyl-1,3-oxazolidin-2-one using a homochiral copper(II) bis(imine) catalyst.⁴²⁹ Capozzi has extended his work on α,α' -dioxo thiones to an asymmetric approach to 1,4-oxathiins.⁴³⁰

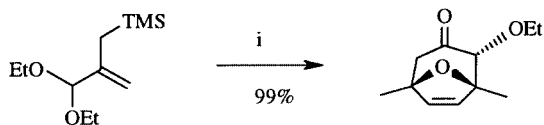


6 [4 + 3] Cycloadditions

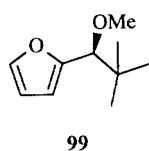
Oxyallyl cations generated from α,α' -dibromo ketones undergo *cis*-endo diastereoselective reactions with furan.⁴³¹ These types of reaction can also be carried out in aqueous milieu.⁴³² Cyclic oxyallyl cations can be used in an approach to tricyclic structures (Scheme 156).⁴³³ Harmata has used allylic acetals as a source of the oxyallyl cation, producing oxabicyclic species functionalised with an alkoxy group (Scheme 157).^{434,435} Barluenga has demonstrated formal [4 + 3] cycloadditions between 2-methyl-1,3-dimorpholinobuta-1,3-diene and Fischer carbene complexes.⁴³⁶ For asymmetric intermolecular reactions, Lautens has used homochiral furan ethers such as **99** to obtain enantiomerically enriched [4 + 3] cycloadducts⁴³⁷ and Kende has used α -chloro imines derived from (*S*)-ethylamines in enantioselective processes (Scheme 158).⁴³⁸ Harmata has used (trimethylsilylmethyl) allylic sulfones (Scheme 159)⁴³⁹ and 2-ethoxyallyl alcohols in intramolecular [4 + 3] cycloadditions,⁴⁴⁰ the latter in a total synthesis of aphanamol.



Scheme 156 Reagents: i, NEt₃, furan, F₃CCH₂OH.

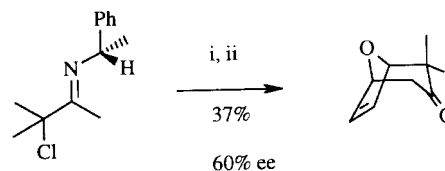


Scheme 157 Reagents: i, furan, TiCl₄, CH₂Cl₂.

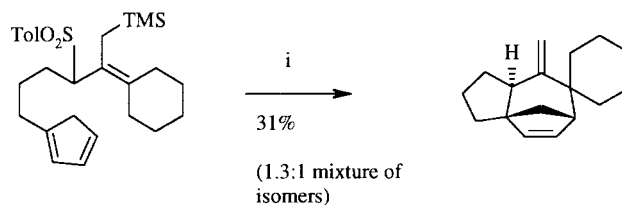


7 [4 + 4] Cycloadditions

Pyran-2-ones attached by a three carbon tether to a furan undergo crossed [4 + 4] cycloadditions to yield novel bi- and tri-cyclic cyclooctanoid systems (Scheme 160).⁴⁴¹ Similarly, a

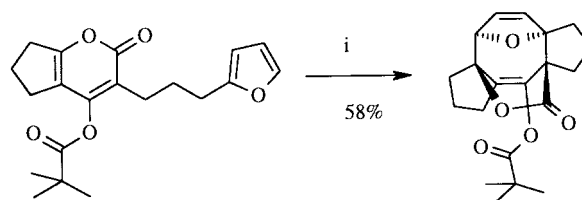


Scheme 158 Reagents: i, AgBF₄, furan, CH₂Cl₂; ii, H₃O⁺.

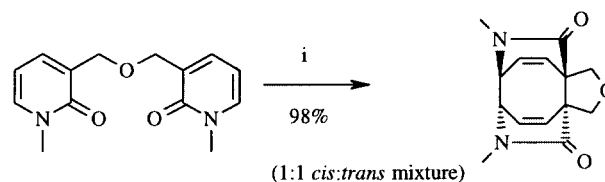


Scheme 159 Reagents and conditions: i, AlMe₃, CH₂Cl₂, -78 °C.

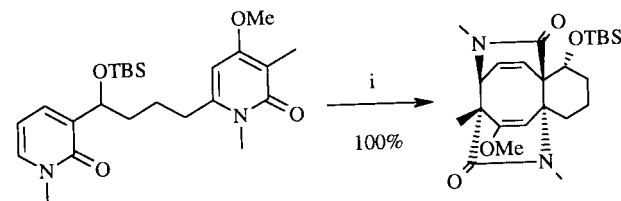
three atom tether linking two pyridones reverses the head-to-tail regioselectivity seen in intermolecular [4 + 4] cycloadditions, yielding the head-to-head cycloadduct (Scheme 161).⁴⁴² Such cycloadducts can be further elaborated by a fragmentation procedure to provide a new synthesis of eleven membered rings.⁴⁴³ In a novel approach, the use of a four carbon tether bearing a pendant silyloxy group allows generation of a photoproduct bearing five stereocentres and both quaternary carbons found in TaxolTM (Scheme 162).⁴⁴⁴ Wender has introduced a transition metal catalysed [4 + 4] approach to fused [5,8] ring systems (Scheme 163).⁴⁴⁵



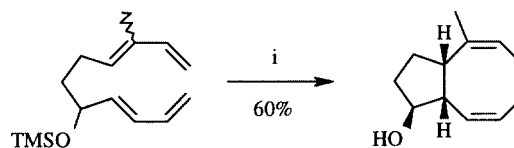
Scheme 160 Reagents and conditions: i, hv, aq. MeOH.



Scheme 161 Reagents and conditions: i, hv, MeOH.



Scheme 162 Reagents and conditions: i, hv, MeOH.

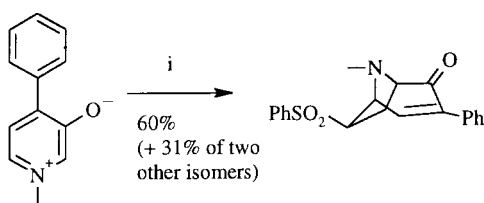


Scheme 163 Reagents and conditions: i, Ni(COD)₂, PPh₃, PhMe, 60 °C.

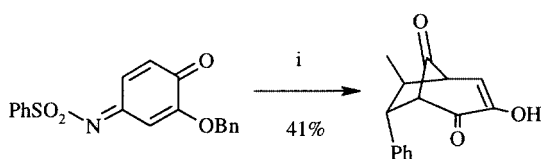
8 [5 + 2] Cycloadditions

Using a pyridinium betaine, Kozikowski has pioneered a [5 + 2] cycloaddition route to 6- and 7-substituted 3-phenyl-

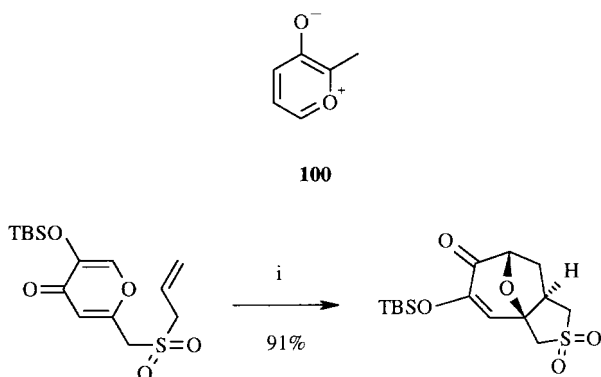
tropanes (Scheme 164).⁴⁴⁶ Benzoquinone monoimides can react with styrenes to produce [5 + 2] cycloadducts (Scheme 165).⁴⁴⁷ Oxidopyriliium salts such as **100** have been used in an approach to the carbon skeleton of the diterpene dictyoxetane.⁴⁴⁸ Intramolecular cycloadditions can readily be achieved by the use of appropriate tethering groups as evidenced by the work of Mascareñas.^{449–451} An example is shown in Scheme 166.⁴⁵¹ Both intermolecular⁴⁵² and intramolecular⁴⁵³ [5 + 2] cycloadditions can be promoted by trimethylsilyl triflate in 3 M lithium perchlorate–ethyl acetate. Engler has published on the use of tandem [5 + 2]/[3 + 2] and [5 + 2]/[3 + 3] sequences that can generate tricyclic structures with up to eight stereocentres.⁴⁵⁴ In asymmetric reactions, Kozikowski has expanded upon his earlier work⁴⁴⁶ to produce an enantioselective route to 2-alkyl-3-phenyltropans using (*R*)-*p*-tolyl vinyl sulfoxide.⁴⁵⁵ Reactions of pyrones tethered to an olefin by a linker containing pendant (–)-8-phenylmenthyl esters are reported to proceed with asymmetric induction.⁴⁵⁶ Perhaps of most interest to the synthetic chemist are the elegant asymmetric approaches to taxanes by Magnus (Scheme 167)⁴⁵⁷ and to phorbol (Scheme 168)⁴⁵⁸ and resiniferatoxin (Scheme 169)⁴⁵⁹ by Wender.



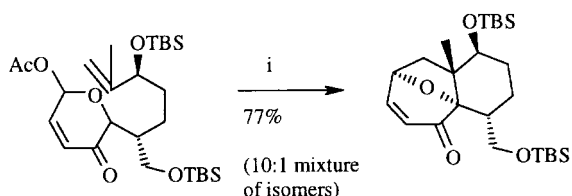
Scheme 164 Reagents and conditions: i, $\text{H}_2\text{C}=\text{CHSO}_2\text{Ph}$, MeCN, Δ .



Scheme 165 Reagents and conditions: i, (*E*)-MeHC=CHPh, TiCl_4 , $\text{Ti}(\text{OPr}^t)_4$, CH_2Cl_2 , -78°C .



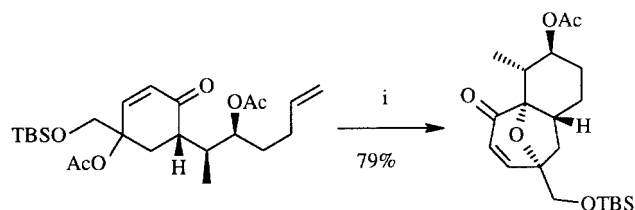
Scheme 166 Reagents and conditions: i, PhMe, 90°C .



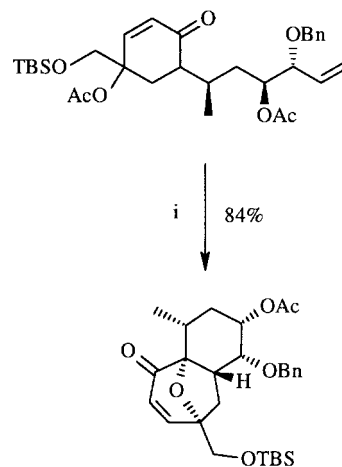
Scheme 167 Reagents and conditions: i, DBU, PhMe, Δ .

9 [6 + 2] Cycloadditions

Rigby has continued his pioneering endeavours in metal-templated [6 + 2] cycloadditions, including construction of

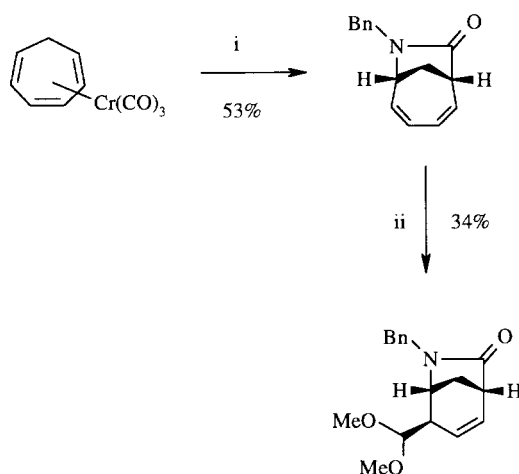


Scheme 168 Reagents: i, DBU, MeCN.



Scheme 169 Reagents and conditions: i, DBU, MeCN, Δ .

6-azabicyclo[3.2.1]octanes (Scheme 170),⁴⁶⁰ an approach to 1,2-disubstituted cyclooctatetraenes (Scheme 171),⁴⁶¹ intramolecular triene/alkyne assembly of various tricyclic units⁴⁶² and an intramolecular [6 + 2] route to β -cedrene (Scheme 172).⁴⁶³ Sheridan has exploited higher order cycloaddition chemistry in an extraordinary tandem [6 + 2]/homo[6 + 2] sequence in which five new carbon–carbon bonds are formed in a single step from a chromium tricarbonyl cycloheptatriene complex plus two different alkynes, generating tetracycloundecadienes (Scheme 173).⁴⁶⁴



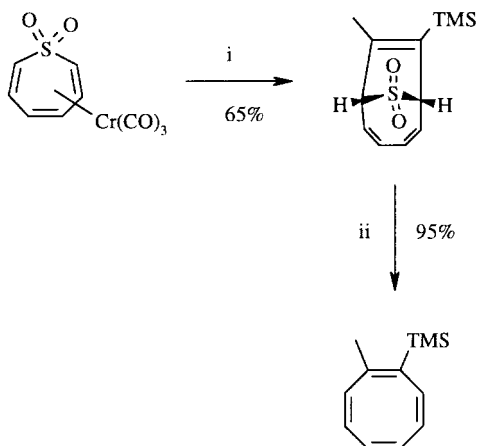
Scheme 170 Reagents and conditions: i, BnNCO, PhH–hexane, hv; ii, $\text{Ti}(\text{NO}_3)_3$, MeOH.

10 [6 + 3] Cycloadditions

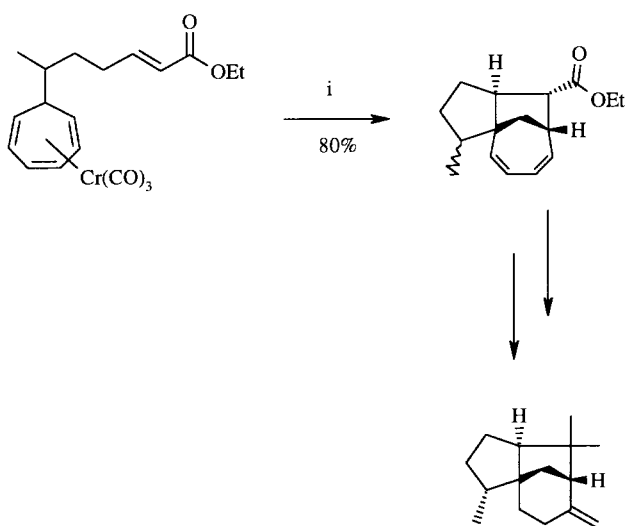
Oxyallyl cations have been reported to add to electron rich fulvene ketene acetals in a [6 + 3] sense (Scheme 174).⁴⁶⁵

11 [6 + 4] Cycloadditions

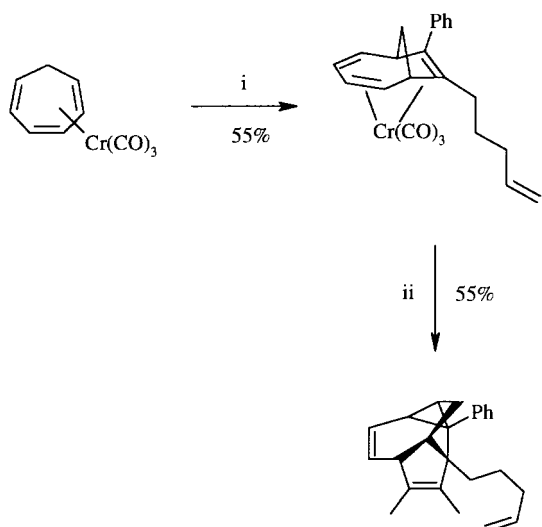
Rigby has exploited higher order photocycloadditions of chromium(0) complexes in a number of areas, for example a sequential [6 + 4] cycloaddition–Ramberg–Bäcklund re-



Scheme 171 Reagents and conditions: i, *hν*, U-glass; ii, *hν*, vycor.

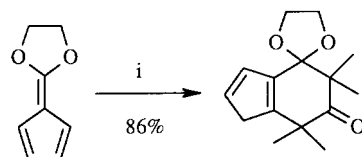


Scheme 172 Reagents and conditions: i, dioxane, 150 °C.

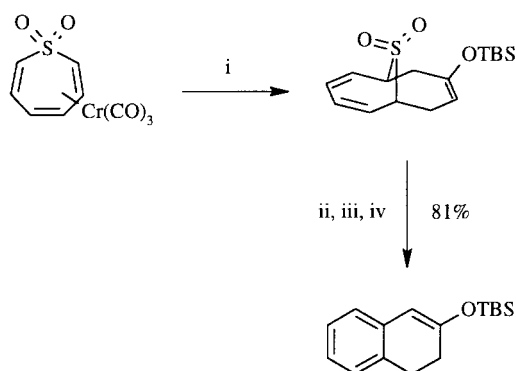


Scheme 173 Reagents and conditions: i, $\text{PhC}\equiv\text{C}(\text{CH}_2)_3\text{CH}=\text{CH}_2$, *hν*; ii, $\text{MeC}\equiv\text{CMe}$, hexane, *hν*.

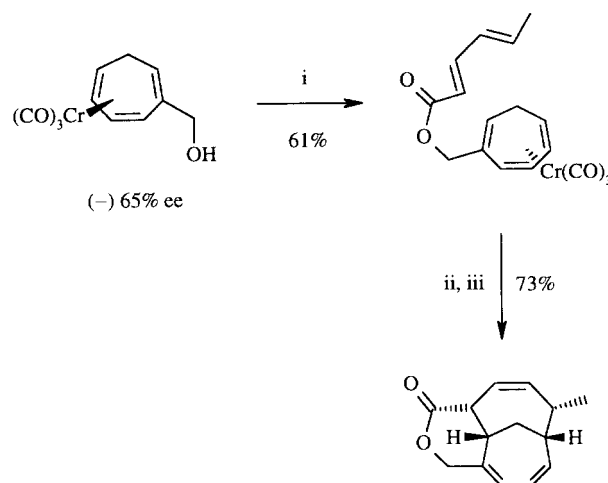
arrangement (Scheme 175),⁴⁶⁶ an approach to the bicyclo-[4.4.1]undecane core structure of the ingenane diterpenes,⁴⁶⁷ catalytic (rather than the normal stoichiometric) metal-promoted reactions,⁴⁶⁸ asymmetric processes involving the use of chiral non-racemic chromium tricarbonyl complexes (Scheme 176)⁴⁶⁹ and lipase-mediated resolution of decomplexed products leading to enantiomerically pure 1,6-methano-



Scheme 174 Reagents: i, $\text{Me}_2\text{C}(\text{Br})\text{COC}(\text{Br})\text{Me}_2$, $\text{Fe}_2(\text{CO})_9$, PhH.

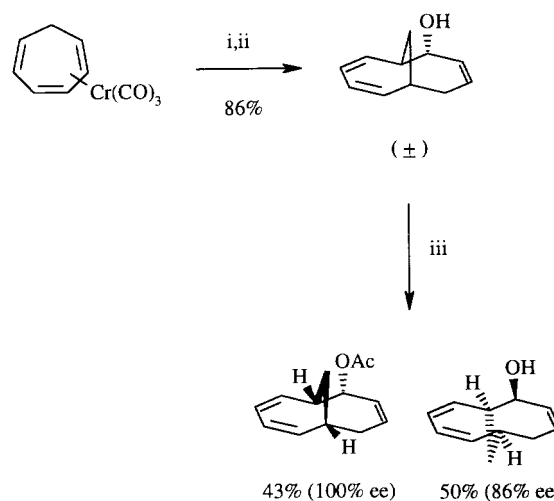


Scheme 175 Reagents and conditions: i, 2-TBSoxybuta-1,3-diene, *hν*, $\text{Cl}(\text{CH}_2)_2\text{Cl}$; ii, KO^tBu , THF, -105 °C; iii, NCS, THF; iv, KO^tBu , THF, -105 °C.



Scheme 176 Reagents and conditions: i, DMAP, CH_2Cl_2 ; ii, *hν*; iii, $\text{P}(\text{OMe})_3$.

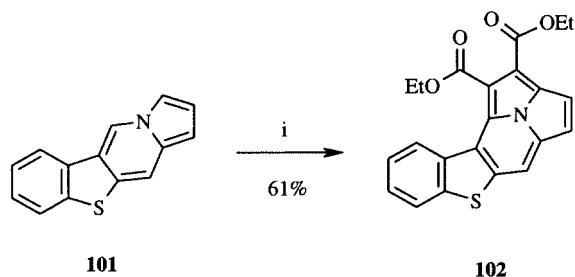
[10]annulenes (Scheme 177).⁴⁷⁰ The first aqueous [6 + 4] cycloaddition has also been reported, involving tropone and 1-(glucopyranosyloxy)buta-1,3-diene.⁴⁷¹



Scheme 177 Reagents and conditions: i, 1-acetoxybuta-1,3-diene, *hν*, hexane; ii, K_2CO_3 , MeOH; iii, PS-30 lipase, isopropenyl acetate.

12 [8 + 2] Cycloadditions

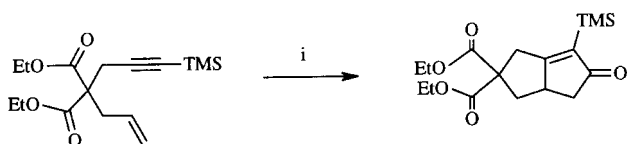
Reaction of cyclopentadiene with an *o*-thiobenzoquinone-methide generated from 2*H*-benzo[*b*]thiete yields an [8 + 2] cycloadduct.⁴⁷² The [1]benzothieno[3,2-*f*]indolizine **101** reacts with diethyl acetylene dicarboxylate, yielding after dehydrogenation the adduct **102** (Scheme 178).⁴⁷³ Acyclic dienes produce novel bicyclo[5.3.0] ring system [8 + 2] cycloadducts on reaction with 3-ethoxycarbonyl-2*H*-cyclohepta[*b*]furan-2-one.⁴⁷⁴



Scheme 178 Reagents and conditions: i, EtO₂CC≡CCO₂Et, PhMe, Δ.

13 [2 + 2 + 1] Cycloadditions

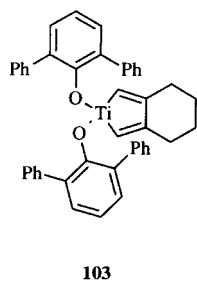
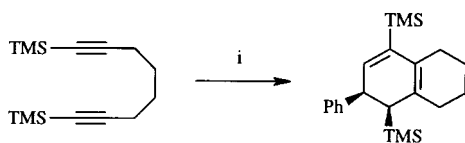
Treatment of 1,6-enynes with catalytic quantities of a ruthenium carbonyl complex and carbon monoxide results in a [2 + 2 + 1] cycloaddition to yield bicyclo[3.3.0]octenones (Scheme 179).⁴⁷⁵



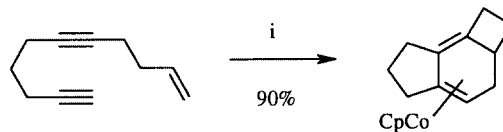
Scheme 179 Reagents and conditions: i, cat. Ru₃(CO)₁₂, 10 atm CO, dioxane, Δ.

14 [2 + 2 + 2] Cycloadditions

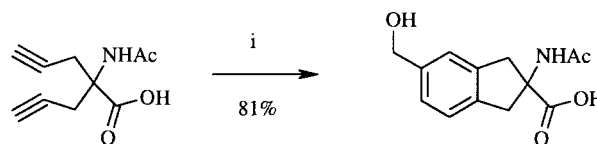
Regio- and stereo-selective synthesis of the cyclohexa-1,3-diene nucleus can be accomplished by a [2 + 2 + 2] cycloaddition catalysed by titanium aryloxides, such as **103** (Scheme 180).⁴⁷⁶ Strained tricyclic dienes can be prepared by cobalt-mediated cyclisation of α,δ,ω -enediynes (Scheme 181).⁴⁷⁷ Using Wilkinson's catalyst, novel indane based amino acids can be synthesised (Scheme 182).⁴⁷⁸ Other uses of [2 + 2 + 2] cycloadditions include cobalt(I)-mediated preparation of annelated substituted bipyridines and terpyridines⁴⁷⁹ and nickel(0)-mediated catalytic asymmetric synthesis of isoindoline and isoquinolines.⁴⁸⁰



Scheme 180 Reagents: i, styrene, **103**.



Scheme 181 Reagents: i, CpCo(H₂C=CH₂)₂, THF.



Scheme 182 Reagents and conditions: i, HC≡CCH₂OH, (Ph₃P)₃RhCl, EtOH, Δ.

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